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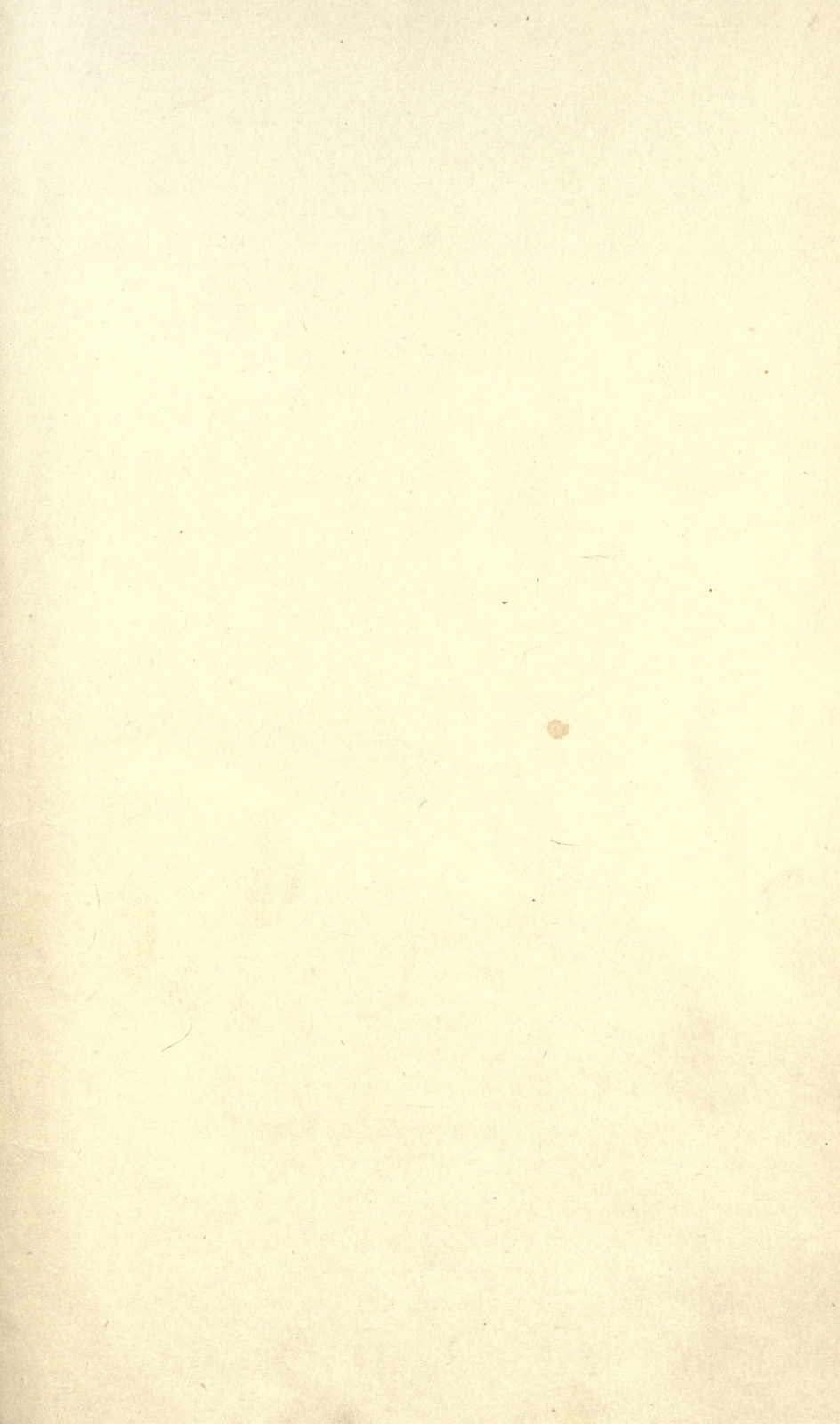
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# LEAD REFINING BY ELECTROLYSIS

BY  
ANSON GARDNER BETTS

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FIRST THOUSAND



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## PREFACE.

THE electrolytic refining of lead bullion has now become an established metallurgical process, with further extensions confidently expected to come from time to time. Lead is almost an ideal metal to refine electrolytically, because its electrochemical equivalent is very high, and hence the power cost is small, and the depositing tanks are relatively smaller or fewer than for other common metals. Its casting into anodes is especially easy, and it stands high enough in the electrochemical scale to leave its impurities almost entirely in the anode slime, as metals, so there is no appreciable contamination of the electrolyte.

The contained information is the result of a number of years of study, experiment and practical work, and is published in the hope that it will save those who may be interested in lead refining practice or its improvement the repetition of experiments already performed, and give them the benefit of the work already done by others and myself. Some space has been devoted to theoretical discussions of conductivity of electrolyte, etc., which I thought would be useful and instructive.

The variety of methods of slime treatment which are discussed in Chapter II, may seem unnecessarily large from the practical standpoint, though I myself believe it is desirable to treat them at the length I have. I had some hesitancy

in including a list of patents published, as they are largely my own, but saw clearly that a treatise on this subject required all available information of any importance, and would be wanted by readers.

I wish to make grateful acknowledgment to my parents, Mr. and Mrs. Edgar K. Betts, of this city, for unfailing assistance and encouragement while performing my experiments. I am indebted for appreciated suggestions and information to Dr. E. F. Kern and Dr. Wm. Valentine, who have been associated with me in developing process and plant, Dr. Kern from April 1902 to June 1904, and Dr. Valentine from October 1902 until now; to Messrs. W. H. Aldridge, John F. Miller, A. J. McNab, and Jules Labarthe of Trail; B. C., Messrs. H. A. Prosser, Aug. E. Knorr and Wm. Thum, of the United States Metals Refining Co., and Messrs. A. S. Dwight and Ernst F. Eurich, and to many others.

TROY, NEW YORK. September, 1907



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# LEAD REFINING BY ELECTROLYSIS.

## CHAPTER I.

### ELECTROLYTES FOR LEAD REFINING.

WHEN two pieces of the same metal are dipped into a solution, no difference of electro-motive force is produced between the metals, as when dissimilar metals like zinc and copper are immersed. When an appropriate solution is used and the pieces of metal (electrodes) are placed in an electric circuit, metal may be dissolved from one electrode and deposited on the other. The quantities of the various metals transported by a certain current in a certain time are proportional to the atomic weight of the metal, divided by the valency in which it exists in the solution (Faraday's law). These quantities are, per ampere hour, for a few metals of interest to lead refining, as follows.

TABLE 1.

Silver.....	4.025	grams	per	amp.	hr.	4.7	amp.	days	per	lb.
Lead.....	3.857	"	"	"	"	4.9	"	"	"	"
Bismuth.....	1.948	"	"	"	"	9.7	"	"	"	"
Antimony.....	1.494	"	"	"	"	12.7	"	"	"	"
Copper (Cuprous).....	2.372	"	"	"	"	7.95	"	"	"	"
Copper (Cupric).....	1.186	"	"	"	"	15.9	"	"	"	"
Tin.....	1.105	"	"	"	"	17.1	"	"	"	"
Iron.....	1.044	"	"	"	"	18.1	"	"	"	"
Gold (Auric).....	2.452	"	"	"	"	7.7	"	"	"	"

As a general thing, by using an appropriate solution, the deposited metal (cathode) is pure, although the dissolved metal (anode) may be very impure, and on this fact electrolytic refining depends.

Solutions containing a salt of the above metals, generally with free acid also present, have been used almost entirely as electrolytes. Some of the metals can be got into alkaline solution, for example, silver, lead, and copper, and some alkaline solutions are used in electroplating, but such solutions are not used in refining, so far.

Only those metals which do not dissolve with evolution of hydrogen on immersion in the refining solution have been successfully refined up to the present time. For metals which cannot be successfully treated wet, as sodium and aluminum, fused electrolytes are used.

The deposition of pure metals depends on the fact that each metal has its own electromotive force of solution. The electromotive force of solution varies a few hundredths of a volt for differences in the concentration of the solution, and is somewhat different for different electrolytes. An approximation is given in Table 2. This table is practically correct for fluosilicate solution.

TABLE 2.

Zinc. ....	+.52 volts
Cadmium. ....	+.16 "
Iron. ....	+.09 "
Lead. ....	-.01 "
Tin. ....	-.01 "
Arsenic. ....	-.40 "
Antimony. ....	-.44 "
Bismuth. ....	-.48 "
Copper (Cupric). ....	-.52 "
Silver. ....	-.97 "
Mercury. ....	-.98 "



The electromotive force of solution may be defined as that difference of voltage which exists between an element and the solution also containing the metal in which it is immersed. An electric current may be flowing in either direction from the electrode and solution, either depositing or dissolving metal, without changing the value of this electromotive force to any more than a slight extent.

The results of this are (1) that with an anode containing a considerable proportion of that one of the metals present in the anode, which stands highest in the series and therefore requires the least application of electromotive force to bring it into solution, only that metal will dissolve, and those lower in the series will remain in the metallic state, and (2) given in the electrolyte a considerable amount of that metal which has the lowest electromotive force of those in the solution, only that metal will deposit, the electromotive force at the cathode being insufficient to deposit the others.

The rule of electrolytic refining is then, that the metals lower in the scale than the principal metal present, are eliminated as metal particles in the anode slime, and the ones higher in the series are eliminated as salts dissolved in the solution or precipitated from it.

The elimination as metal in the anode slime is the best of the two, as an increasing concentration of other metals in the solution requires a change of electrolyte, which is troublesome. For instance, in electrolytic silver refining, the principal impurity, copper, dissolves from the anode and collects in the solution, while the percentage of silver gets less.

Lead, on the other hand, stands higher in the scale than all the impurities it contains in appreciable quantities, so that

the solution does not need to be changed. Taking this into consideration, with the great ease of casting lead into anodes, and melting cathodes, the comparatively large quantity transported by the current, so that a relatively small amount of power is necessary and the production is rapid, lead has the most favorable physical and electrochemical constants for electrolytic refining of all the common metals.

With an anode of composite metals, we do not have, in general, a mixture from which one or more metals may be dissolved, leaving the other metal or metals in the pure state, but a mixture of different compounds of the metals between themselves. The electromotive force of solution of lead combined with antimony for example, is less than that of pure lead. The result is that in the electrolytic refining of alloys we do not have the full difference in electromotive forces of the metals available for making a complete separation. The difference in electromotive force between lead and the impurities is though, considerable enough to leave something remaining after allowing for the combining force of lead and the impurities. The strength of these combinations varies from practically no combination in the case of lead and copper to quite a considerable one in the case of lead and antimony.

The transport of a pure metal from one pure electrode to another in the same physical condition, through a solution, requires very little energy, provided time is no object. The metal of the anode may be, though, in a harder or softer condition, or may not be the simple metal, but may rather consist of a series of compounds with other metals present as impurities. The elements in these compounds and aggregations in general are so weakly united, that usually the energy



requirement for their decomposition per ton of anode is practically negligible. An exception may be noted in the case of lead-antimony alloys, "hard lead"; to extract the last of the lead from the antimony requires an e.m.f. of over .2 volt. The nature of these compounds is of interest as the anode slime probably consists of a mixture of them.

The question of time is, however, one of the most important factors, for the refining capacity of a plant of given size varies inversely with the speed of working. As we can only afford to use a reasonable amount of electric energy per ton refined, the first consideration is to find an electrolyte of as high an electric conductivity as possible.

The best conducting electrolyte will be found with a melted salt, and melted lead chloride is an exceptionally good conductor.

At 580° C., according to Kohlrausch,  $\text{PbCl}_2$  has a resistance of .0373 ohms for a column 1 sq. decimeter by 1 decimeter = .095 ohms per column 1 sq. inch by 1 inch. For comparison, the aqueous electrolyte used with a resistance of 1.3–1.4 ohms is about fourteen times a poorer conductor. With the fused electrolyte and the same voltage and separation of electrodes, the current density would be about 210 amperes per square foot, a 4000 ampere vat requiring then about 19 sq. ft. of surface. The expenditure of 1–1.5 kilowatt would not keep an apparatus of this size, or of one anywhere nearly as large, at a red heat, and  $1\frac{1}{4}$  kw. is about all the power used for a 4000 ampere tank. It is doubtful if one kw. would keep an apparatus occupying more than a few cubic inches at the necessary temperature.

Fused lead chloride dissolves lead sulphide and also gives a low melting, high-conductivity electrolyte, which, how-

ever, could not be as good as lead chloride alone. Lead fluoride I have tried to use as an electrolyte in decomposing lead sulphide, but it is relatively infusible.

Lead chloride melts at a moderate heat, stated in places to be about  $500^{\circ}\text{C}$ . Provided a suitable tank could be found, if it was attempted to use fused lead chloride with the usual depending electrodes, of course they would melt off, and the loss of heat would be enormous too.

Mr. R. H. Sherry made an experiment in my laboratory with a mixture of fused zinc and lead chloride, melting below the melting-point of lead, so that solid lead electrodes could be used. The resistance of zinc chloride is given by Kohlrausch as 10.98 ohms per cubic decimeter, = 27.9 per cubic inch. The resistance in Mr. Sherry's experiment was at  $310^{\circ}\text{C}$ . about 2.5 ohms per cubic inch, or greater than the aqueous electrolytes.

Special apparatus would have to be devised and the current density would have to be far increased beyond the 10–15 amperes per square foot used with solutions, to reduce the radiating and heat-conducting cross-sectional area sufficiently, and this increase of current strength would offset to a greater or less degree, probably greater, the advantage of high conductivity.

Special apparatus has been devised or suggested by Borchers\* and Ashcroft† for refining lead with fused electrolytes.

The use of a mixture of lead chloride and oxy-chloride was proposed by Prof. Borchers,\* the idea being that such a mixture does not attack iron, while the chloride does. The

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\* *Electrometallurgy*, 1st English Edition, page 338.

† *Electrochem. and Metal Ind.*, Vol. IV (1906), page 357.



crude lead was allowed to flow from groove to groove down one side of an iron vessel as anode, with an iron cathode at the other side, from which the deposited lead ran down to a separate collecting space. Prof. Borchers stated that the result in refining lead and bismuth alloys was excellent, which I can well believe as far as the chemical result is concerned, but that is probably about the only use to which the process could be put. After the lead has been largely removed from this particular anode metal it is as fusible and liquid as before, if not more so, but ordinary crude lead and bullion on the other hand would get thicker and less fusible from the accumulation of copper and arsenic, silver and antimony, and would soon be too thick to be handled in this way, long before a large part of the lead could be removed. Further, it would take some experimental labor to determine whether all the impurities were separated, notably the arsenic and antimony. It is also to be much doubted whether the power cost could be bought as low as by the wet process.

Ashcroft has proposed to make the melted lead alloy, contained in a pot, anode, and spin a cathode of metal above the surface of the anode, and very near it. The lead deposited on the cathode is to remain suspended by the action of a magnetic field, instead of dropping back into the anode metal. The magnetic field is to rotate the conducting cathode, which it might do, but the action on the lead on the underside of the cathode, if there were any action in practice, could not act to support this lead, but only to move it in a horizontal circle, the same as the cathode itself.

There will be a difficulty in making the surface of the anode metal lie flat, as the metal will tend to move in a circle too, from friction and perhaps from magnetism in connection

with the current passing through. The same trouble I mentioned before with the impurities of the lead will also appear here, to a more serious extent, as the impurities are lighter than lead, and as the lead was removed would form a scum on its surface.

The inevitable difficulty with the accumulating impurities of the lead in such methods and other serious difficulties, made the wet method always seem the best. Since the power cost per ton of lead with the cheap electric power now available (and this will probably be cheaper as time goes on), is only about 50 cents, a great saving is not possible anyway.

The historical development of electrolytic lead refining, up to my own work, is given by Messrs. Watt and Philip in their book, "Electroplating and Electrorefining."\*

Prof. N. S. Keith as early as 1878 developed his process of refining lead, with an electrolyte containing 180 grams sodium acetate per litre, in which was dissolved 18.5 to 22.2 grams of lead sulphate per litre. He used 20 lb. anodes, 15×24 inches, and  $\frac{1}{8}$  to  $\frac{3}{16}$  inches thick, wrapped in muslin cloths to catch the anode slime, which would otherwise drop to the bottom of the tank with the refined lead crystals falling from the cathodes.

At Rome, N. Y., a plant was built with 30 tanks producing 3 tons of lead per day of twenty-four hours. The tanks were circular, made of a kind of concrete mixture, 6 feet in diameter, 40 inches deep, with a central pillar 2 feet in diameter occupying the centre of the tank. Brass cylindrical cathodes were used 2 inches apart, and extended all the way round the tank, with 270 anode plates to the tank 6×24

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\* New York and London, 1902.



inches, and weighing 8 lbs.; current was supplied by an Edison dynamo of 2000 amperes and 10 volts. The anodes were hung from a frame which rotated continuously and carried scrapers that scraped the deposited lead from the cathodes. The current density, calculated from these figures, was 3.2 ampères per square foot.

Tommasi\* published various articles in 1897 and 1898 describing his arrangement for refining lead, also with the acetate solution. His proposition was to use as a cathode a circular aluminum-bronze disc, mounted on a shaft just above the top of the electrolytic cell, which disc was to turn once a minute, and be relieved of its deposit of spongy lead by a scraper above the tank, while the spongy lead was automatically carried off to a press. Tommasi, in elaborate but wrong calculations, presumes a refining cost of 8.6 francs per metric ton with steam power and 5.8 francs with water power. The process described would, however, probably cost nearer 50 or 75 francs, if all went well.

L. Glaser† reports a number of experiments with little exactness of description, in depositing lead from various electrolytes, the description being limited to lead nitrate, lead nitrate and sodium nitrate, lead acetate, sodium nitrate saturated with lead hydrate, and caustic potash with lead hydroxide in solution of various strengths, and claims a solid lead deposition. I have repeated Glaser's experiments very fully as far as it is possible to follow him, and in no case was I able to get a solid deposit of any measurable thickness.

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\* Comptes Rendus, 1896, Vol. 122, p. 1476. Zeitschrift für Electrochemie, Vol. 3, 92, 310, 341.

† Zeitschrift für Electrochemie. 1900, Vol. 7 (24), 365-369 and (26) 381-386.

Following a work of Foerster and Guenther, who offered the explanation that spongy zinc deposits are caused by the simultaneous deposition of zinc oxide with the zinc, Glaser attempts to prove the cause of the loose lead deposit to be due to the co-deposition of lead hydroxide. This is, however, incorrect theory, as anyone can easily see by electrolyzing lead solutions containing free acid, as nitric, acetic, fluosilicic, etc., which by their acidity absolutely prevent the separation of lead hydroxide, and yet give loose deposits. It is also possible, without making any alteration of the acidity of a proper solution, to cause the separation of a solid instead of incompact deposit, as will be seen later.

The next proposition for refining lead is seen in patent specifications.\* I refined about half a ton of lead, in 4-cells each  $10\frac{1}{2}$ " wide, 16" deep, and 30" long, containing 9 anodes weighing about 12 lbs. each, and  $10\frac{1}{4}$  inches wide by  $13\frac{1}{4}$  inches deep. The strength of the solutions varied from 4 to 20 grams lead and 12 to 25 grams  $\text{SiF}_6$  per 100 cc., but the deposit was always incompact. The cathodes consisted of sheet iron, which it was attempted to coat with lead by dipping into lead in a deep pot, and afterward by lead-plating them. In the first experiments the idea was to simply melt the lead off the iron when the cathodes were finished, by dipping into melted lead, after which the cathodes could be returned to the tanks. In the later experiments the cathodes were greased and the lead afterward peeled off mechanically.

Every few hours during the runs, which lasted during the

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\* U. S. Patents, A. G. Betts; 679,357, July 30, 1901; 679,824, August 6, 1901.



day time for about a week, with a current from 120-150 amperes (=7 to 8.8 amperes per square foot, total e.m.f. per cell 0.175 volts), the cathodes were taken out and passed through steel rolls of about 3" diameter. The sheets came through the rolls in quite a solid deposit and with a smooth surface. A good deal of electrolyte was squeezed out and part of this was lost, and the whole was a disagreeable job with the machinery at hand. A sample of the deposit, which seemed quite solid, showed a specific gravity of 10.28 only, against 11.36 to 11.40 for pure lead. This would mean a loss of electrolyte in the remaining pores, per ton refined, of about .3 cubic foot, still a rather serious item.

The idea was to equip the tanks, as may be seen from the above-mentioned patents, with a pair of rails on each side, over which ran a machine that automatically stopped over each cathode in succession, raised it through a pair of rolls and returned it to its position in the tank.

TABLE 3.

## ANALYSES OF BULLION TREATED AND REFINED LEAD PRODUCED.

	Bullion.		Refined Lead.		Slime.
Ag about	.50%	Ag	.0003%	Ag	36.4%
Cu "	.31%	Cu	.0007%	Cu	25.1%
Sb "	.43%	Sb	.0019%	Sb	29.5%
Pb "	98.76%	Pb	99.9971%	Pb	9.0%

	Bullion.		Refined Lead.
Cu. ....	.75 %	Cu	.0027%
Bi. ....	1.22 %	Bi	.0037%
As. ....	.936 %	As	.0025%
Sb. ....	.6832%	Sb	.0000%
Ag. ....	358.89 oz.	Ag	.0010%
Au. ....	1.71 oz.	Au	None
		Fe	.0022%
		Zn	.0018%

The idea of using rails at the side of the tanks, over which carriages may be run to carry electrodes in and out and slime out, seems to be one that might be adopted in refineries with some advantage.

The objection to a loose mass of separate lead crystals, as previously invariably produced in electrolyzing lead solutions, is serious from the refining standpoint. After doing considerable work with mechanical methods of compacting the lead, I discovered certain materials that, if added to such a solution as the fluosilicate, caused the production of solid lead deposits, notably gelatine and pyrogallol, although when added to acetate solutions they had no valuable effect. As gelatine is the cheapest, it alone has been adopted in practice. Saligenin and resorcin were found to cause an improvement, but not quite so solid a deposition as the other two. The search was not limited to organic reagents, but they alone were found suitable. With the addition of small amounts of gelatine to a fluosilicate solution, perhaps 1 part of gelatine to 5000 or less parts of solution, the lead separates as a solid smooth deposit, with a specific gravity of 11.3 to 11.4, the same as cast lead.

The way in which the gelatine, etc., bring about this remarkable result is hard to trace. I am satisfied that the next step toward a complete explanation is to be found in variation in hardness or tensile strength of the cathode deposit resulting from the use of gelatine, etc. The principal reasons for this opinion are based on these facts:

1. \* Although equally pure, the solid electrolytic lead deposit is several times stronger than ordinary lead.

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\* Betts, Trans. Am. Electrochem. Soc. Vol. VIII, 1905, page 83.



2. The greater the tension at the surface of an electro deposit, the greater the tendency to keep the new surface forming smooth.\*

3. Lead deposited from liquids in which its surface tension after immersion must be greater, is smoother, *e.g.*, pyridine solutions.†

4. Strong metals, otherwise suitable for electro-deposition, give the smoothest deposits. Weak metals give loose crystalline growths.

In what way the gelatine or other similar addition acts to increase the strength of the surface layer of cathode deposit has not been definitely established.

It is an interesting fact that the addition of gelatine or pyrogallol to the acetate and similar solutions does not cause the production of a solid deposit, while the addition of gelatine in the strong-acid solutions, fluosilicic, fluoboric, etc., does.

Snowdon claims to mechanically produce solid lead from the acetate solution by the use of a rapidly revolving cathode, but does not give the specific gravity of the product.‡

I criticize the practice of describing lead deposits as solid, homogeneous, etc., without making any definite statements as to the specific gravity, mechanical soundness, etc. Some definite standard is required to show how "solid" a deposit is, also the thickness of the deposit should be detailed. Many deposits of slight thickness have quite a smooth and solid appearance for that reason, but after building them up a little more, their true loose nature can be recognized.

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\* Betts, Trans. Am. Electrochem. Soc. Vol. VIII, 1905, page 85.

† Kahlenberg, Trans. Am. Electrochem. Soc. Vol. VI, 1904, page 40.

‡ Trans. Am. Electrochem. Soc. Vol. IX, 1906, page 221.

The lead deposit forming in lead fluosilicate-fluosilicic acid solutions, containing .1% of gelatine, and five or more per cent lead, is smooth and solid, and thick pieces cut from the deposit show a specific gravity of 11.35 to 11.40; the same metal after melting and casting shows practically the same specific gravity, in some cases exactly the same. With a little more lead, say 7-8%, and the average current density employed in commercial operations of 15 amperes per square foot, the resulting cathodes, after reaching a considerable thickness, are smoother. The electrochemical equivalent of lead is so high that with only 5% lead, the layer in the immediate neighborhood of the cathode is probably nearly exhausted in respect to lead, and if the lead is allowed to go much below 4%, a black, slimy deposit of lead is the result.

That gelatine does not affect the current efficiency I determined some years ago in the following way. Two solutions were electrolyzed in series, one containing gelatine and the other without.

TABLE 4.

Experiment No.	Without Gelatine.		With Gelatine.	
	Weight Deposited.	Weight Dissolved.	Weight Deposited.	Weight Dissolved.
1	4.06 gr.	4.06 gr.	4.04 gr.	4.06 gr.
2	24.70 gr.	24.89 gr.	24.72 gr.	24.90 gr.

The electrodes were arranged to be weighed without removing them from the solution at all, to avoid the disturbing influence of air oxidation on the spongy deposit from the solution with no gelatine.

The amount of lead transported by the current has been

made a careful study.\* Under the most perfect conditions yet applied to the deposition of lead, the electrochemical equivalent of lead is found to be 103.43, that is, the atomic weight of lead corresponding is 206.86 and the amount of lead transported per ampere hour is 3.857 grams.†

For refining lead, we require a solution of as high a conductivity as is commercially available, which also will contain at least several percent of combined lead without being saturated with the lead salt. Certain acids, such as fluosilicic, fluoboric, dithionic, various fatty sulphuric acids, as ethyl-sulphuric acid, and phenol-sulphonic and benzene sulphonic acids, have been found to meet the requirements of high electric conductivity and solubility of their lead salts.

For a comparison of the conductivity of these acids with the acetate electrolytes of Keith and Tommasi, see Table 5.

TABLE 5.

In 100 c.c. Solution.	Name.	Temperature.	Approximate Resistance per Inch Unit.
7.7% Pb ( $C_2H_3O_2$ ) <sub>2</sub> . . . . .	Acetate. . . . .	19.6° C.	75 ohms.
‡14.5% Pb ( $C_2H_3O_2$ ) <sub>2</sub> . . . . .	Acetate. . . . .	19.4° C.	58 “
5 gr. Pb, 7 gr. BF <sub>4</sub> . . . . .	Fluoborate. . . . .	25 ° C.	4 “
5 gr. Pb, 15.7 gr. C <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> . . .	Benzenesulphonate..	25 ° C.	2.7 “
5 gr. Pb, 12.5 gr. C <sub>2</sub> H <sub>5</sub> SO <sub>4</sub> . . .	Ethylsulphate. . . . .	25 ° C.	3.6 “
5 gr. Pb, 9.5 gr. C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> . . . . .	Acetate. . . . .	25 ° C.	84 “
15.7 gr. Pb, 2.4 gr. K, and 21.4 gr. C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> . . . . .	Acetate. . . . .	26 ° C.	22 “

Considerations of cost so far have required the use of fluosilicic acid, but dithionic acid may yet be found to be more economical.

Several recent writers have apparently thought that fluosilicic acid had some peculiar property that made it better

\* Betts and Kern, Trans. Am. Electrochem. Soc. Vol. IV, 1904, page 67.

† F. W. Clarke, Trans. Am. Chem. Soc. Vol. XXVIII, 1906, page 307.

‡ Kalender für Elektrochemiker, 1903. Neuberger.



than other acids for giving a solid lead deposit. Mr. Senn\* in his paper describes experiments to see if it was also suitable for refining cadmium, and obtained some excellent results with fluosilicate of cadmium, and H. Mennicke† has applied the acid to refining tin and obtained good results. These views are, however, probably incorrect. The true suitability of an acid is more dependent on its strength, and solubility of its salts, than on other things.

Messrs. Senn and Mennicke would probably have done equally well with other non-oxidizing acids having an equal strength and forming salts of cadmium and tin respectively, of equal solubility.

Prof. Ostwald in his work "Outlines of General Chemistry," translated by Dr. James Walker, New York, 1890, page 360, gives a valuable table and makes this statement in connection with it.

"The fact stated by Hittorf that the power of reaction and the electrolytic conductivity are always concurrent properties, speaks at once in favor of this assumption. [That the strength of an acid is a definite and definable characteristic proportional to its dissociation.] It obtains further support from the circumstance that the processes of electrolytic conductivity and of chemical decomposition both depend on the molecules under consideration falling into smaller sub-molecules; without this decomposition there can neither be a new distribution of parts as in chemical reaction, nor a transport of electricity attached to the ions, as in conduction.

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\* Zeitschrift für Electrochemie. II (1905), 229-245.

† Zeitschrift für Electrochemie. XII (1905), 112, 136, 161, 180.

"But the most decisive and telling argument for the soundness of the assumption is the numerical agreement of the values for the chemical activity on the one hand and the electric conductivity on the other. The numbers on pages 354 and 356 for the rate of catalysis of methyl acetate and of the inversion of cane sugar, agree so closely with those representing the relative electric conductivity, that there cannot exist the slightest doubt of the intimate connection between the two series.

"In the following table there is tabulated under I. the electric conductivity of normal solutions of acids, under II. the coefficients of velocity for the catalysis of methyl acetate, and under III. the coefficients of inversion of cane sugar.

TABLE 6.

Acid.	I.	II.	III.
1. Hydrochloric, $\text{HCl}$ . . . . .	100	100	100
2. Hydrobromic, $\text{HBr}$ . . . . .	100.1	98	111
3. Nitric, $\text{HNO}_3$ . . . . .	99.6	92	100
4. Ethanesulphonic, $\text{C}_2\text{H}_5\text{SO}_3\text{OH}$ . . .	79.9	98	91
5. Isethionic, $\text{C}_2\text{H}_4\text{OH}\cdot\text{SO}_2\text{OH}$ . . . .	77.8	92*	92
6. Benzenesulphonic, $\text{C}_6\text{H}_5\cdot\text{SO}_2\text{OH}$ .	74.8	99	104
7. Sulphuric, $\text{H}_2\text{SO}_4$ . . . . .	65.1	73.9†	73.2
8. Formic, $\text{H}\cdot\text{COOH}$ . . . . .	1.68	1.31	1.53
9. Acetic, $\text{CH}_3\cdot\text{COOH}$ . . . . .	.424	.345	.400
10. Monochloracetic, $\text{CH}_2\text{Cl}\cdot\text{COOH}$ . .	4.90	4.30	4.84
11. Dichloracetic, $\text{CHCl}_2\cdot\text{COOH}$ . . . .	25.3	23.0	27.1
12. Trichloracetic, $\text{CCl}_3\cdot\text{COOH}$ . . . .	62.3	68.2	75.4
18. Lactic, $\text{C}_2\text{H}_4\text{OH}\cdot\text{COOH}$ . . . . .	1.04	.902	1.07
25. Oxalic, $(\text{COOH})_2$ . . . . .	19.7	17.6	18.6
29. Tartaric, $\text{C}_2\text{H}_2(\text{OH})(\text{COOH})_2$ . . .	2.28	2.30	
32. Citric, $\text{C}_3\text{H}_4\text{OH}(\text{COOH})_3$ . . . . .	1.66	1.63	1.73
33. Phosphoric, $\text{PO}(\text{OH})_3$ . . . . .	7.27	—	6.21
34. Arsenic, $\text{AsO}(\text{OH})_3$ . . . . .	5.38	—	4.81

\* Should be .98 }  
 † Should be 54.7 } as on page 354 of Ostwald's book.

We are especially interested in the strength of fluosilicic acid, fluoboric acid, and dithionic acid, as well as some of those given in the table.

Mr. R. H. Sherry made determinations of the strength of these by the methyl-acetate method as described in Ostwald's same book, page 352, and also made tests on HCl and  $\text{H}_2\text{SO}_4$  as a check. His results cannot be directly added to Ostwald's table, as they were made at different temperatures and a different amount of methyl-acetate was used.

He used normal solutions of  $\text{H}_2\text{SiF}_6$ , that is, containing 7.2 gr.  $\text{H}_2\text{SiF}_6$  per 100 cc.; normal solution of dithionic acid, 8.3 grams  $\text{H}_2\text{S}_2\text{O}_6$  per 100 cc.; normal sulphuric acid 4.9 grams per 100 cc.; normal hydrochloric acid 3.65 grams HCl per 100 cc. Through an error  $1\frac{3}{4}$  N fluoboric acid was used instead of normal, and the only basis of comparison made was with  $1\frac{3}{4}$ N HCl. Normal fluoboric acid = 8.8 grams  $\text{BHF}_4$  per 100 cc.

The figures give the amount of acetic acid liberated in grams in 90 minutes and are very nearly proportional to the strength of the acids.

TABLE 7.

At Approximately 26° C.				At 26.5 – 27° C.	
N $\text{H}_2\text{SO}_4$	N $\text{H}_2\text{SiF}_6$	N HCl	N $\text{H}_2\text{S}_2\text{O}_6$	$1\frac{3}{4}$ N HCl	$1\frac{3}{4}$ N $\text{BHF}_4$
(a) .2330	(a) .2540	(a) .4106	(a) .4223	(a) .5541	(a) .5450
(b) .2387	(b) .2578	(b) .4116	(b) .4169	(b) .5568	(b) .5391

We then get approximately the ratios of the following table, taking normal HCl = 100:



TABLE 8.

1. Hydrochloric acid, $\text{HCl}$ .....	100
2. Dithionic acid, $\text{H}_2\text{S}_2\text{O}_6$ .....	102
3. Fluboric acid, $\text{BHF}_4$ .....	95
4. Fluosilicic acid, $\text{H}_2\text{SiF}_6$ .....	62
5. Sulphuric acid, $\text{H}_2\text{SO}_4$ .....	57
6. Acetic acid, $\text{HCH}_3\text{CO}_2$ .....	.345
7. Ethyl sulphuric, $\text{C}_2\text{H}_5\text{SO}_4\text{H}$ .....	74
8. Benzene sulphonic, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ .....	74

In other tables in his book Professor Ostwald gives the strength of benzene-sulphonic acid and ethyl sulphuric acid, as determined by the methyl acetate method, as practically 100. The figures in this table are for determinations made by the electric conductivity method. I do not think the methyl acetate method is reliable for acids having an organic residue on account of the naturally greater dissolving power such acids must possess even in solution, for organic substances as methyl acetate. Such determinations certainly do not check anyway with the conductivity determinations.

In recent experiments, all these strong acids have been made up into lead-depositing electrolytes containing 4 grams and more of lead per 100 cc. beside free acid, giving lead deposits of varying characteristics, but all of them always loose and crystalline and unsuitable for practical work, on account of their lack of solidity and the short circuits produced. All the electrolytes in the following list and many others, too, have produced loose deposits without exception.

A partial list of electrolytes used for depositing lead is given in Table 9, the figures being for grams per litre.

TABLE 9.

400	grs. lead nitrate		
60	grs. lead nitrate,	33 grs. sodium nitrate,	6 grs. nitric acid
250	grs. lead nitrate,	35 grs. sodium nitrate,	6 grs. nitric acid
350	grs. lead nitrate,	35 grs. sodium nitrate,	6 grs. nitric acid
33	grs. lead nitrate,	33 grs. sodium nitrate,	6 grs. nitric acid
33	grs. lead nitrate,	100 grs. sodium nitrate,	6 grs. nitric acid
100	grs. lead nitrate,	400 grs. sodium nitrate,	6 grs. nitric acid
530	grs. lead acetate,	117 grs. ammonium acetate,	33 grs. acetic acid.
400	grs. sodium nitrate saturated with lead hydrate		
5.6	grs. caustic potash saturated with lead hydrate		
448	grs. caustic potash saturated with lead hydrate		
50	grs. lead, 87 grs., $\text{BF}_4$		
50	grs. lead, 157 grs. benzene sulphonic acid radicle		
50	grs. lead, 125 grs. ethyl sulphuric acid radicle		
27	grs. lead formate, 46 grs. formic acid		
60	grs. lead acetate, 60 grs. acetic acid		
32.5	grs. lead acetate, 60 grs. acetic acid, 60 grs. potassium acetate.		
186	grs. lead lactate, 93 grs. lactic acid		
186	grs. lead lactate, 186 grs. lactic acid		

With the addition of gelatine to the strong acid solutions (fluosilicic, fluoboric, dithionic, organic sulphuric and sulphonic acids), they give solid lead deposits, the best of which have been obtained with fluosilicic and fluoboric acids, and on one occasion, when the solution happened to be in just the right condition, with dithionic acid. Benzene-sulphonic acid gives the roughest deposits and is the most troublesome to use. The lead salt is not very soluble.

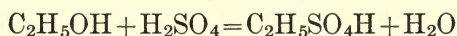
A number of these deposits of considerable thickness have been examined for specific gravity from time to time, with these results:

TABLE 10.

Fluosilicate. ....	11.29	11.35	11.36
Benzenesulphonate. ....	11.35	11.37	
Ethyl sulphate. ....	11.27	11.31	
Fluoborate. ....	11.39		
Dithionate. ....	11.20		
Phenolsulphonate. ....	11.35		

*Phenol-sulphonic acid* gives an excellent lead deposit, as does benzene disulphonic acid and phenol disulphonic acid. All the other organic sulphonic acids that I tried, as toluene and naphthalene sulphonic acids, give altogether too insoluble lead salts. Methyl- and amyl-sulphuric acid are practically equivalent to ethyl-sulphuric acid. Ethane disulphonic acid, from  $C_2H_4Br_2$  and ammonium sulphite by Strecker's reaction, gave too insoluble a lead salt.  $COCl_2$  and a sulphite solution did not give the expected dioxy methylene disulphonic acid. Calcium carbide and concentrated sulphuric acid gives a number of sulphonic acids, but I have not investigated this reaction to a great extent.

With tax-free alcohol there is a slight chance of economically using *ethyl-sulphuric acid*. The reaction between alcohol and sulphuric acid is



and provides a relatively cheap acid for refining lead. Ethyl-sulphuric acid in strong solution decomposes, however, again into alcohol and sulphuric acid. I accordingly determined the decomposition rate of a solution I had, which contained 10 grams lead and 8.8 grams free  $C_2H_5SO_4H$  per 100 cc. This solution deposited about .03 grams lead sulphate per day, at about  $25^\circ C$ . This corresponds to about 2.1 lbs.  $C_2H_5SO_4H$  decomposed per ton lead refined. To prepare 2.1 lbs. of the acid would require about 1 lb. alcohol and 2 lbs. fuming  $H_2SO_4$  (30%  $SO_3$ ). The alcohol would cost at least 4 cents and the sulphuric acid 2.5 cents, or a total cost per ton lead for these materials of 6.5 to, say, 10 cents. The above solution was pretty weak, however, and the tem-



perature a little low, so I think it would be found with such a solution as would be used practically, that the decomposition would be three or more times as great. The resistance of this solution of lead ethyl sulphate and ethyl sulphuric acid (10 grams lead and 8.8 grams  $\text{C}_2\text{H}_5\text{SO}_4\text{H}$  per 100 cc.) was at  $27^\circ\text{C}$ ., 2.6 ohms per cubic inch as against about 1.4 ohms for the regular fluosilicate solutions.

Solutions of lead phenol-sulphonate gave excellent results as far as conductivity and solid lead deposition went, but the solution seemed to be unstable for a crystalline deposit kept forming for a long time. The sulphonation of the phenol takes place readily and good yields may be obtained. 20 grams of phenol were heated up to  $180^\circ\text{C}$ . for one hour with varying quantities of  $\text{H}_2\text{SO}_4$ . With 25 grams  $\text{H}_2\text{SO}_4$ , titration of the product with sodium carbonate, showed that the reaction was nearly quantitative. With more sulphuric acid, considerable disulphonic acid was obtained, about 30% of the monosulphonic acid being converted to disulpho-acid, when 40 grams  $\text{H}_2\text{SO}_4$  were used for 20 grams phenol.

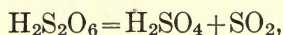
A solution containing 75% mono-acid and 25% di-acid and 30 grams lead in 100 cc., of the following composition: lead 30 gr.,  $\text{C}_6\text{H}_5\text{SO}_3'$  28.4 gr., and  $\text{C}_6\text{H}_4(\text{SO}_3)_2''$  15.2 gr. per 100 cc. gave a resistance per cubic inch of 2.04 ohms.

The solution was practically neutral and the resistance would no doubt have been much less with more free acid. However, the relatively high cost of pure phenol, and the difficulty I found in trying to get a suitable solution from crude phenol or cresol, led to the abandonment of these experiments, although they looked promising at first.

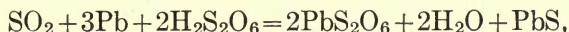
Lead benzene-sulphonate is relatively little soluble and

the lead deposit was poor. It is also more difficult to get even a fair yield of benzene sulphonic acid.

Many tests have been made with *dithionic acid* electrolytes, and on one occasion a very excellent deposit was got. All the other experiments have given a rather poor deposit. The surpassing conductivity of dithionic acid, the fact that the only raw material actually necessary to make it is  $\text{SO}_2$  which so many works have plenty of and to spare, make it seem almost an ideal electrolyte. The acid is subject to decomposition, however, in strong or warm solution, as follows:



both the products of reaction being bad. The sulphuric acid precipitates lead sulphate into slime, but worst of all, the  $\text{SO}_2$  is reduced by the cathode, forming lead sulphide.



which spoils the cathode deposit, if deposited in any quantity. The one good deposit I mentioned probably resulted from the use of a solution freshly made up with crystallized lead dithionate, water, and dilute sulphuric acid to precipitate out part of the lead and set free some of the dithionic acid, which contained no  $\text{SO}_2$ .

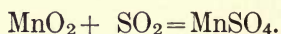
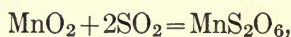
I had experiments made lasting for several week's continuous run with another solution, but the deposit was "door-mat" to the last, but I am not satisfied that the solution, if used properly, cannot be made to yield an excellent deposit.\*

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\* Since the above was written further experiments have also failed to give an entirely satisfactory deposit continuously.

The rate of decomposition is quite slow. A solution containing 6.6 grams Pb and 5.75 grams free  $\text{H}_2\text{S}_2\text{O}_6$ , or a total of 10.75 grams  $\text{S}_2\text{O}_6$  per 100 cc., giving a resistance per cubic inch at  $26.5^\circ\text{C}$ . of 1.92 ohms (a fluosilicate solution of corresponding acidity would be about 2.6–2.7 ohms), decomposes at the rate of complete decomposition of the  $\text{S}_2\text{O}_6$  in about 80 weeks, or from 1.75 to 2.2 lbs.  $\text{H}_2\text{S}_2\text{O}_6$  decomposed per ton of lead refined. Another solution containing 7.5 grams lead and 14.4 grams  $\text{S}_2\text{O}_6$  per 100 cc., decomposed in  $5\frac{1}{2}$  months at the rate of total decomposition in 36 years. The conductivity of a solution containing 7.5 grams Pb and 12.6 grams  $\text{S}_2\text{O}_6''$  per 100 cc. at  $21\frac{1}{2}^\circ$  was 1.75 ohms.

The preparation of the dithionic acid we used was accomplished in two different ways. In each case  $\text{MnO}_2$  was dissolved in water by a current of  $\text{SO}_2$  gas passed through. Two reactions may take place as follows, of which the first is the only useful one:



Conditions favoring the first are low temperature, say  $10^\circ\text{C}$ ., and the continual presence in the solution of an excess of  $\text{SO}_2$ . Under these favorable conditions the yield has been as high as 86% of the manganese dissolved converted to dithionate and 14% to sulphate, or a yield of 93% on the  $\text{SO}_2$  used. In another case the yield on sulphur was 81.6%, and on manganese dissolved 63.3%. The reaction between the manganese dioxide and  $\text{H}_2\text{SO}_3$  is rapid.

At first the manganese salt was decomposed with lead peroxide:  $\text{MnS}_2\text{O}_6 + \text{PbO}_2 = \text{MnO}_2 + \text{PbS}_2\text{O}_6$ . It was soon



found that while this reaction was all right when sulphates were absent from the solution, the yield was poor otherwise. We accordingly precipitated the  $\text{SO}_4$  first by adding lead dithionate from a previous batch. It was thought that the manganese dioxide precipitate could be used over and over again, but the precipitated dioxide will not give nearly as good a yield as native pyrolusite.

Only certain varieties of lead peroxide will react with the lead solution. The peroxide precipitated by heating a mixed solution of lead acetate and calcium hypochlorite, did very well, but the cost would be too high for practical work, so I devised an electrolytic method as follows: By electrolyzing a solution of common salt with carbon cathode and lead anode, lead hydrate is precipitated, especially well if the solution is heated a little. If the mixture is then electrolyzed with carbon anode and lead cathode, sodium hypochlorite is produced, which converts the lead hydrate into lead peroxide. The original idea was to merely reverse the current occasionally, but that did not do very well because there was always a coating on the lead anode, and when the current was reversed the coating was again reduced to spongy lead with a corresponding loss of efficiency. The difficulty was surmounted by using two sets of electrodes in different parts of the cell, and even then there was difficulty with the formation of a coating on one of the electrodes, but an observation of Dr. Kern that the coatings fell off if the current was interrupted entirely for a short time occasionally, put us in possession of a practicable process of preparing the precipitated lead peroxide from lead anodes by the help of electricity. The product was entirely free from  $\text{Pb}(\text{OH})_2$  if the proportion of the two sets of reactions we were carrying on

were so adjusted that there was always excess of NaOCl formed.

The other method of preparation is based on treating the manganese dithionate and sulphate solution with slacked lime, giving a solution of the calcium salt, and a precipitate containing the manganese, which could perhaps be used equally as well or better than the original  $\text{MnO}_2$  ore used, in a Spiegeleisen or ferromanganese furnace, thus paying for the manganese. The calcium salt was decomposed with sulphuric acid for calcium sulphate and dithionic acid. I had experiments made in my laboratory on this process, but the results do not show anything for or against its probable success.

*Fluoboric acid* is a somewhat better conductor than fluosilicic acid, if the comparison is made on the basis of equal neutralizing power, in about the ratio 3 to 2 for weak solutions, the difference becoming less as the solutions become stronger. The amount of HF required to produce the acids in the ratio for equal acidity, is 80 to 61. For weak solutions for a given amount of fluorine, a slightly greater conductivity can be secured by the use of boric instead of silicic acid.

For the relatively stronger acids that must be used for economical reasons, the advantage is with fluosilicic acid, both in amount of HF required and in cost of silicic acid as against boric acid. Thus a solution containing 5 gr. Pb and 15 gr.  $\text{BF}_4'$  per 100 cc. has a resistance at  $30^\circ \text{C.}$  of about 1.4 ohms, and a solution with 5 gr. Pb and 16.3 gr.  $\text{SiF}_6''$  per 100 cc. (each containing 13.1 gr. F) has a resistance of about 1.3 ohm, per inch  $\times$  inch<sup>2</sup> unit.

Considering the higher cost of boric acid used as raw

material, these figures lead to the conclusion that fluosilicic acid is considerably the best.

Fluosilicic acid is soluble in water and decomposable by alkalis into alkali fluoride and silica. Even as weak a base as litharge will effect a decomposition, which is the reason white lead and not litharge is used in making the lead salt. Heating causes a loss of acid by volatilization if the acid is strong.

According to Baur,\* Stolba noticed in 1863 that if fluosilicic acid is boiled down the residue will dissolve silica, therefore  $\text{SiF}_4$  must have escaped in boiling. The author (Baur) has found it to be the case that an acid containing 13.3%  $\text{H}_2\text{SiF}_6$  gives a distillate also containing  $\text{H}_2\text{SiF}_6$ . Weaker acids give distillates with excess of HF, stronger acids with excess of  $\text{SiF}_4$ . If then concentrated  $\text{H}_2\text{SiF}_6$  is distilled partly, without silica being present, the residue should be capable of dissolving silica; if weak acids 5-10% are evaporated, silica should deposit. This is found by experiment to be the case. The relative amounts of steam and hydrogen and silicon fluorides escaping are not given by the author.

The specific gravity of fluosilicic acids is given in Table 11, taken from Comey's "Dictionary of Solubilities," originally given by Stolba.

The preparation of lead fluosilicate solution from fluosilicic acid can be successfully carried out in at least two ways. The most convenient method is to add lead carbonate or white lead, which dissolves with effervescence.

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\* Berichte, Deutsch. Chem. Ges. 1903. 36 (16), 4209, abstracted Jour. Soc. Chem., Vol. 27, page 17.



TABLE 11.

Per Cent $\text{H}_2\text{SiF}_6$	Specific Gravity.	Per Cent $\text{H}_2\text{SiF}_6$	Specific Gravity.
2	1.0161	20	1.1748
4	1.0324	22	1.1941
6	1.0491	24	1.2136
8	1.0661	26	1.2335
10	1.0834	28	1.2537
12	1.1011	30	1.2742
14	1.1190	32	1.2951
16	1.1373	34	1.3162
18	1.1559		

In his paper Mr. Senn\* describes an experiment in which he added to 100 grams of 19.2%  $\text{H}_2\text{SiF}_6$ , 100 grams of lead as white lead, and got a precipitate containing 83.3%  $\text{PbF}_2$  and 16.68%  $\text{SiO}_2$ . This is of course the result when a great excess of lead is used, which is not, however, a matter of practical importance. Practically in making lead fluo-silicate solution, little or no precipitate is formed.

Perhaps a cheaper method, though a less convenient one, is to electrolyze the solution with lead anode and cathode, separated by a diaphragm. I made up about 10 cubic feet of solution experimentally, in fact this was the first method used. The solution was brighter and whiter and gave a better deposit on the start than that made in the other way. It also happened to contain an excess of HF. The solution was stored in carboys, and it finally dissolved the glass and ran out. Yet the excess of HF did not cause any precipitation of  $\text{PbF}_2$  when the solution was used in refining.

In using this method, the lead anodes dissolved evenly, the e.m.f. of the cell was about  $1\frac{1}{4}$  volts, and no precipita-

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\* Zeitschrift für Elektrochemie, April 14, 1905.

tion was formed. A very little black spongy lead deposited on the cathodes, with much hydrogen. That the HF present did not precipitate lead fluoride, is due to the fact that HF is relatively a weaker acid than  $\text{H}_2\text{SiF}_6$ , and  $\text{PbF}_2$  is not entirely an insoluble salt. The saving made by using lead as raw material instead of white lead, and apparatus to be used, are treated on pages 243 and 244. The apparatus used in making the solution is also shown in Fig. 1.

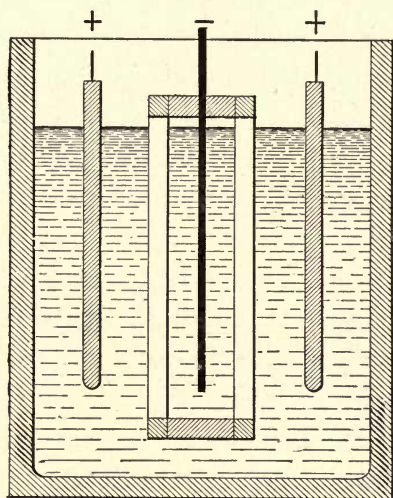


FIG. 1.

The crystallization of lead fluosilicate is a difficult matter. The best results are got by placing a strong, nearly neutral solution over sulphuric acid under a bell jar and giving the solution several weeks to concentrate and crystallize, when beautiful crystals are obtained. The evaporation of the solution even at 40–50° C. causes the precipitation of a fine crystalline product of inexact composition, not entirely soluble in water. Crystals have also been got by dissolving lead

and lead peroxide in very strong fluosilicic acid and lead fluosilicate solutions, from two electrodes connected together through a resistance.

Lead-fluosilicate crystallizes in very soluble, brilliant crystals, resembling those of lead-nitrate, and containing four molecules of water of crystallization, with the formula  $\text{PbSiF}_6 \cdot 4\text{H}_2\text{O}$ . This salt dissolves at  $15^\circ \text{C}$ . in 28 per cent of its weight of water, making a syrupy solution of 2.38 sp. gr. Heated to  $60^\circ \text{C}$ ., it melts in its water of crystallization. A neutral solution of lead-fluosilicate is partially decomposed on heating, with formation of a basic insoluble salt and free fluosilicic acid, which keeps the rest of the salt in solution.

The electrolysis of fluosilicic acid and probably also of fluosilicates, is not entirely a simple electrolysis in which the ions  $\text{H}'$  and  $\text{HSiF}_6'$  take part. There is a tendency toward decomposition into  $\text{SiO}_2$  and  $6\text{HF}$ , the reverse of its formation. Late experiments indicate that this takes place to some considerable extent, but for the most part the  $\text{HF}$  liberated at the cathode and the silica at the anode recombine under the influence of circulation and diffusion. An excess of  $\text{HF}$  in the solution would obviously tend to prevent the formation of silica, and a solution containing excess of silica would deposit silica in the anode slime until a condition of equilibrium was arrived at, when no more silica would deposit. There is a certain loss of fluosilicic acid in actual practice which I regard is mostly due to mechanical loss by leaks, etc., because the silica in the slime is generally about 2% only, or about

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\* Betts and Kern, Trans. Am. Electrochem. Soc., Vol. 6, page 67. Clarke, Am. Chem. Soc.

† F. W. Clarke, Jr., Am. Chem. Soc., 28, 306, 190.

‡ Private communication from the management.



one pound per ton of lead, corresponding to 2.3 pounds of  $\text{H}_2\text{SiF}_6$  decomposed. Solution has been thought to dissociate into which HF evaporates into the air, while the corresponding silica remains in the slime. The actual amount of HF present in the solution is usually slight, and its evaporation must be very small, on account of small vapor tension and high combining power with water. The fumes produced in a closed tank-room, refining perhaps 70 tons of lead daily, on the supposition that the acid is lost in the air to the extent of 100 to 300 or more lbs. fluorine in the form of  $\text{SiF}_4$  and HF per day, would make the air unbearable, whereas the actual condition is that there is no noticeable acid fume in the air even in winter with the building closed. I cannot, therefore, believe that appreciable quantities of acid are lost by evaporation from the tanks.

There is always, of course, a considerable mechanical loss in the large bulk of slime, in the pores of the cathodes, and on the surface of both cathode and anode scrap, and from leaks in the tanks. New tanks absorb some solution and the salt  $\text{PbSiF}_6$  probably crystallizes in the wood, which also causes a loss with new tanks. In view of these facts and also analyses of slime, the loss of acid by electrolytic decomposition not offset by the reaction between the  $\text{SiO}_2$  and HF formed is probably extremely small.

That silica deposits on anodes from solutions containing fluosilicic acid has been proved by electrolyzing solutions of ferric sulphate containing fluosilicic acids and analyzing the slimy coating on the anode in a similar experiment, and by the electrolysis of ferrous fluosilicate;\* in both cases with an insoluble carbon anode.

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\* Private communication. Aug. E. Knorr.

In either case silica deposits on the anode, whereas if  $\text{H}_2\text{SiF}_6$  was not decomposable in solution no such thing would occur. In his article "Zur Kenntniss der Elektrolytischen Bleiraffination," H. Senn also described an experiment in which he electrolyzed fluosilicic acid with platinum electrodes, when silica separated.

"EXPERIMENT 40.—I used as electrolyte fluosilicic acid of specific gravity 1.267 (36.7 gr.  $\text{H}_2\text{SiF}_6$  per 100 cc.). This contained a little hydrofluoric acid. Electrodes: platinum. Anode surface: 36.8 sq. cms. Cathode surface 41.6 sq. cms. Current: 0.45 amperes. Tension: 2.7 volts. Time 19 hrs.

"At the close of the research the anode and the bottom of the glass were covered with a layer of gelatinous silica. The electrolyte had the peculiar smell of hydrofluoric acid. This had attacked the glass. Since I had no method of determining hydrofluoric acid in presence of fluosilicic acid, I had to be content with a qualitative proof.

"The fluosilicic acid I filtered off and found in 250 cc. of electrolyte .1841 grams  $\text{SiO}_2$ , corresponding to .4401 grams  $\text{H}_2\text{SiF}_6$ . This decomposition is indeed a result of the fact that  $\text{SiF}_6$  was discharged on the anode."

That the silica should deposit on the anode rather than on the cathode is a little surprising at first. If there is a dissociation of  $\text{H}_2\text{SiF}_6$  into HF and  $\text{SiO}_2$ , as some have thought, HF is so much more a conductor than  $\text{SiO}_2$  that it would apparently go to the anode to a greater extent than  $\text{SiO}_2$ , and at the anode there would be an excess of HF, not  $\text{SiO}_2$ .

In the experiment of Senn's the proportion of silica deposited corresponds to a decomposition of 0.48% of all the  $\text{H}_2\text{SiF}_6$  present, and as the glass was attacked, some or all of this must have come from the glass. In this experiment

there may have been a good deal more decomposition than this, as the continual circulation would bring the anode and cathode products together again, when the original equilibrium from formation of  $\text{H}_2\text{SiF}_6$  would be again established.

The maximum chemical and mechanical loss cannot be more than 6 lbs. of  $\text{H}_2\text{SiF}_6$  per ton of lead deposited, for analyses of a solution, thoroughly mixed both before and after a certain 150 tons of lead was deposited with a current density of 10–12 amperes per square foot, showed only this amount of loss. The solution contained 15%  $\text{SiF}_6$  and about 6% Pb. Any greater loss than this, observed when working at this current density, must then be an avoidable mechanical loss, as indeed part of this 6 lbs. loss must have been.

A sample of Trail slime from regular running, analyzed by me, contained 2.2%  $\text{SiO}_2$  including silica in  $\text{H}_2\text{SiF}_6$  present. The slime of course is not completely washed over, and part or all of this silica then is due to the electrolyte not washed out. This shows a maximum loss in slime of about 2.1 lbs.  $\text{H}_2\text{SiF}_6$  per ton lead, occurring at the time that particular slime was made. Even part of the apparent loss is in some cases the result of deposition of excess of silica present in the solution used.

Solutions of fluosilicic acid may contain excess of silica, and it is probable that  $\text{H}_2\text{SiOF}_4$  is formed to at least a slight extent, while after in use some time they probably contain excess of HF. In all cases the amount of the unstable compounds in solution will vary with the concentration, temperature, etc. For that reason I think determinations of silica in anode residues from lead refined with new solutions are not reliable as indicating the extent to which  $\text{H}_2\text{SiF}_6$  is decomposed, nor what a lead fluosilicate solution will do after



it has practically reached its condition of equilibrium. H. Senn gives a few illuminating analyses in his paper which show the point I am making.

TABLE 12.

Experiment Number.	SiO <sub>2</sub> in Slime.
28	24.87%
30	25.12%
34	1.82%
35	1.26%
36	.9%

It will be noted that the large proportion of SiO<sub>2</sub> was found in slime from new solution.

Starting with a solution which will deposit silica in the slime, while the ratio of Si to F in the solution gradually becomes less, ultimately a condition of equilibrium will be reached for any given constant conditions of temperature, current density, strength of solution, etc.

Just at what point equilibrium will be reached, that is when the power of the solution containing free HF or H<sub>2</sub>SiF<sub>6</sub>, capable of combining with silica to form H<sub>2</sub>SiF<sub>4</sub>O or H<sub>2</sub>SiF<sub>6</sub>, is exactly balanced by the tendency of the current to deposit silica on the anodes is impossible to say, and on account of the constantly varying conditions it is not apt to be determined.

However, equilibrium will be reached long before the solution can contain so much free HF that PbF<sub>2</sub> can precipitate or other undesired reactions occur. With an ordinary solution, say 7 grams Pb and 16 grams SiF<sub>6</sub> per 100 cc. as much as 5% free HF may be present without precipitating PbF<sub>2</sub>. That is, the acidity due to HF may be as high as that due to free H<sub>2</sub>SiF<sub>6</sub> without precipitating PbF<sub>2</sub>, of course on account of the fact that H<sub>2</sub>SiF<sub>6</sub> is relatively a much stronger

acid than HF, and is able to decompose a limited amount of insoluble  $\text{PbF}_2$ .

Evidently if a start is made with a particular solution, the slime may very easily contain a good deal of silica on the start, until equilibrium is reached, but this does not mean a loss of valuable fluorine, but of relatively valueless silica. On the other hand, by having a certain amount of free HF present, the slime can contain no precipitated silica. In practice very high silica in the slime, say 15%, is apt to be obtained on the start with a new solution.

Evidently the surface of the cathodes, anode scrap, and metal particles of the slime that must be taken from the solution and wetted by it, is quite large. On account of the ease with which slime can be broken up and washed, the loss in the slime can be reduced to almost any extent. The surface of the anode scrap and cathodes can also be freed from acid to any extent by washing, but if there are any pockets of solution in the cathodes, or any chemical combination of lead with the electrolyte, as in copper deposited from the acetate solution under certain conditions,\* such losses would be unavoidable.

To investigate the losses practically resulting from electrolyte carried off by the cathodes, six pieces of cathodes from a large pile were obtained from the United States Metals Refining Company's Grasselli plant, and analyzed as follows: Samples of 100-150 grams were dissolved slowly while warming only slightly in dilute nitric acid, of which only a rather small excess was used. A very little water-glass solution was added to the dilute acid on the start, to insure that the

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\* "Ueber das Acetatkupfer." Carl Benedicks. Metallurgie, 1907 (4) 5.

fluorine present would be combined as  $\text{SiF}_6$ . The water-glass dissolved entirely, but during the solution of the lead some silica separated. This was filtered off, the free nitric acid nearly neutralized with caustic potash (by alcohol) and a large excess of potassium nitrate and acetate added. The

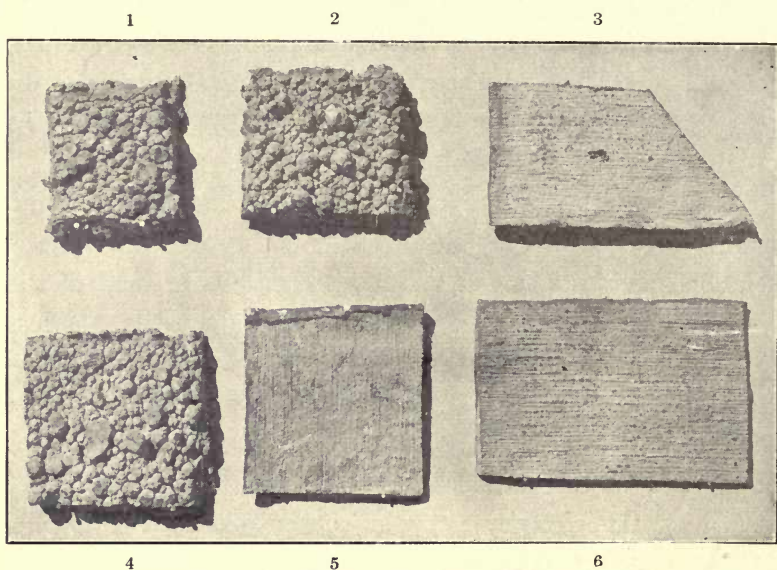


PLATE 1.—SAMPLES OF LEAD CATHODES.

precipitated  $\text{K}_2\text{SiF}_6$  was filtered off and titrated, giving the following results. The photographs show the lead pieces from which the samples were cut, one photograph showing one side and the other photograph the other side.

TABLE 13.

Number in Photograph.					
1.....	.015%	$\text{SiF}_6$	0.30 lb.	$\text{SiF}_6$	per ton lead.
2.....	.011%	"	0.22	"	" " " "
3.....	.005%	"	0.10	"	" " " "
4.....	.009%	"	0.18	"	" " " "
5.....	.002%	"	0.04	"	" " " "
6.....	.003%	"	0.06	"	" " " "



We have evidently a very small loss of acid in the cathodes, and I have been informed that results similar to mine have been obtained at the Trail refinery.\*

The method of washing cathodes in use when the above pieces were made was to wash them with water first, and use

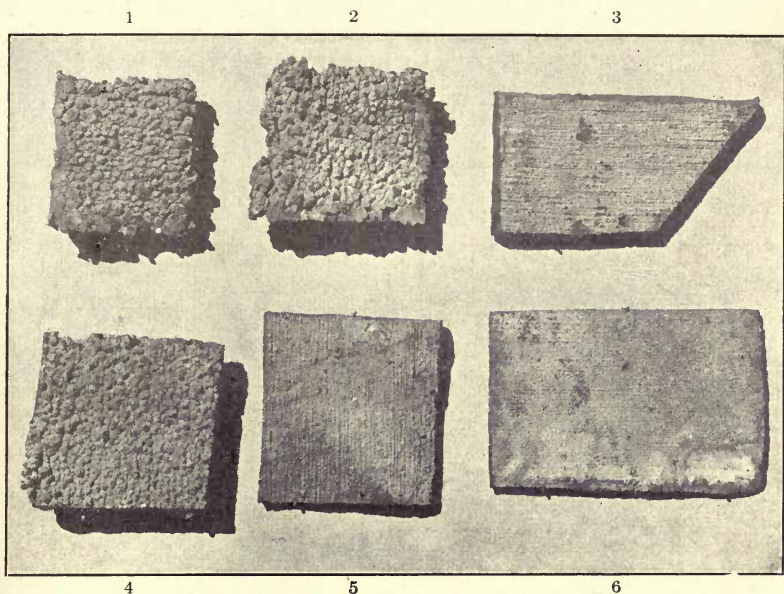


PLATE 2—SAMPLES OF LEAD CATHODES.

the wash-water over and over until nearly of the same strength as the main electrolyte, when the wash-water is added to the electrolytic tanks. The average loss from acid solution remaining on the cathodes after draining is evidently about one-half the loss involved if the electrolyte was merely allowed to drain off. To determine just what this loss might be, samples 2, 4, 5, and 6 in the photographs, were cleaned of a surface coating of white lead, and weighed after wetting and draining for a minute or two, and again after becoming dry, with the result given in Table 14.

\* Letter from Mr. W. H. Aldridge.

TABLE 14.

Number in Photo-graph.	Weight Cathode per Square Foot.	Solution on Cathode.	Acid Loss per Ton Lead.	Average Loss in Practice.	Remarks.
2	28.8 lbs.	0.50%	1.66 lbs. $\text{SiF}_6$	0.83 lbs. $\text{SiF}_6$	Cathode average weight and roughness.
4	22 lbs.	0.39%	1.33 lbs. $\text{SiF}_6$	0.67 lbs. $\text{SiF}_6$	Cathode average weight and roughness.
5	16 lbs.	0.36%	1.20 lbs. $\text{SiF}_6$	0.60 lbs. $\text{SiF}_6$	Unusual cathode.
6	11 lbs.	0.22%	0.76 lbs. $\text{SiF}_6$	0.38 lbs. $\text{SiF}_6$	Unusual cathode not well wetted.

The above cathodes were deposited from a solution containing 8% Pb, and are solidier than those obtained with a solution containing 6% Pb, as used at Trail, which may account somewhat for the higher acid loss at Trail.

The maximum loss, with fairly solid cathodes of average thickness, of 28 to 30 lbs. per square foot, is not greater than 1 lb.  $\text{SiF}_6$  per ton lead. The loss on anode scrap cannot be over 30 to 40% of this amount, on account of smaller surface (1 anode makes 2 cathodes usually) and smoother surface both.

The loss in slime may be reduced by a moderate amount of washing to 2 lbs.  $\text{SiF}_6$  per ton lead or lower. The loss outside of leaks, which can of course vary extremely, and evaporation from the tanks which cannot be otherwise than negligible, when the air in the tank-room has no acid smell, as is usually the case, cannot then be over 3.5 lbs.  $\text{SiF}_6$  per ton. If more than this, something is wrong with the plant, which might be due to a bad leak or not sufficient washing of the slime, or deposition of soft rotten lead on the cathodes or other less evident causes.

The acid loss at Trail in 1902 and early in 1903 was as given in Table 15.

TABLE 15.

Aug. 3—Sept. 16,	245	tons deposited	13.8 lbs. $\text{SiF}_6$ per ton deposited.
Sept. 16—Oct. 6,	120	" "	7.7 " " " "
Jan. 22—Feb. 13,	135-145	" "	6.3 " " " "

The solution was, however, weaker than is used at present, as follows:

TABLE 16

Aug. 3,	7.86% Pb	10.58% $\text{SiF}_6$
Sept. 16,	6.19% "	7.94% "
Oct. 6,	6.07% "	6.93% "
Jan. 17,	6.40% "	8.56% "

On the other hand during at least the first two of the above periods, no evaporation of wash-water was practised, and only enough was used in a crude way to make up for the solution taken out. There were leaks, too, and no suitable apparatus for catching a good share of them.

The average amperes and volts at the time may be seen from Table 17.

TABLE 17.

Average.				Current Efficiency.			
Aug.	1-15	3393 amps.	.293 volts per tank	59 %	12.8	amps. per sq. ft.	
"	15-31	3196 "	.328 " " "	90 %	12.1	" " "	"
Sept.	1-15	3406 "	.39 " " "	72½ %	12.9	" " "	"
"	15-30	3148 "	.42 " " "	74 %	11.9	" " "	"
Oct.	1-15	2724 "	.44 " " "	89½ %	10.6	" " "	"
"	15-31	2593 "	.435 " " "	92 %	9.8	" " "	"
Nov.	1-15	2247 "	.435 " " "	81½ %	8.5	" " "	"
"	15-30	1891 "	.42 " " "	93 %	7.2	" " "	"

The apparent heavy loss for the first period was probably due to absorption by the new tanks, leaks, and the unsettled condition of everything, but principally the solution was not well mixed, for the sample indicates considerably more acid than was actually purchased by the plant. The loss



for the third period, with a weaker electrolyte, however, shows better work than is reported at present. Before January 17th some new acid had been added. It would appear that the high acid makes much higher acid loss, but that conclusion is not safe, as other conditions were changed very much during the first few months.

The actual loss of acid experienced at the Trail refinery up to the present, I have been informed by the management, is about 10 lbs.  $\text{SiF}_6$  per ton lead. Probably this has been improved since the figure was determined some time ago.

Tables 18 and 19 give the electrical resistance of acid lead fluosilicate solutions. Table 18 is from determinations by Dr. E. F. Kern in my laboratory. The other table gives older determinations made by myself, and includes many solutions of no practical importance, but at the time the table was made it was not known which solutions would be most desirable. The temperature coefficients are obtainable from Table 19. The conductivity of the solutions are also plotted as Figs. 2, 3, and 4.

The amount of gelatine required under good working conditions is not great, and may be taken at from  $\frac{1}{2}$  lb. to  $\frac{3}{4}$  lb. per ton of lead deposited. Gelatine in the form of glue is always used, as it is cheaper. I believe the better grades of glue the most suitable, for some of the cheapest glue makes a disagreeable smell in the tank-room. In practical work, when the glue in the solution is about used up, and it is necessary to use more, there will be noticed on the cathodes a tendency toward the formation of points on the lumps, which are readily noticeable with a little practice. The glue is added in the form of a hot, strong solution, and may be best put in the circulation-tank a little at a time.

The appearance of the pure lead fluosilicate solution is that of a colorless liquid. After it has been in use for some time, it has sometimes acquired a greenish tinge from traces of iron and perhaps nickel in the lead anodes. If the solution is allowed to stand in contact with air away from the reducing action of the electrodes, it acquires a brownish yellow color, which at first was thought to be a ferric salt, but now I believe it is due to a coloring-matter introduced with

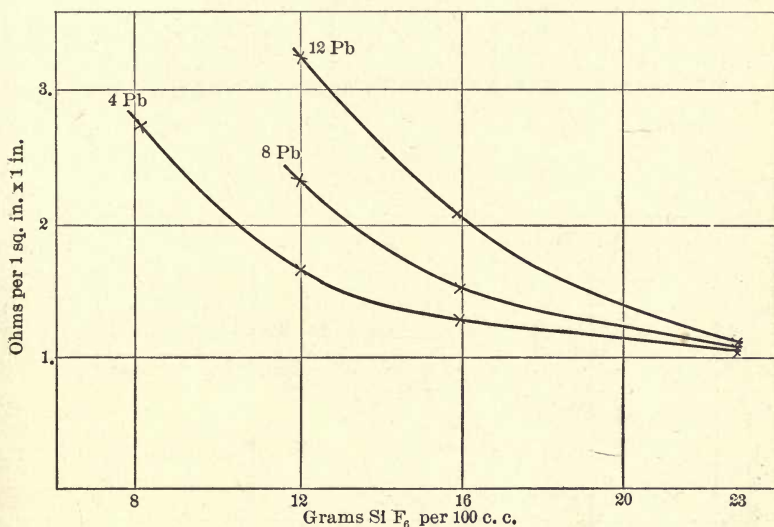


FIG. 2.

the glue. On again using the solution for refining it becomes colorless again, due probably to the reduction of the coloring-matter to the reduced or "leuco" condition, which is a characteristic of most organic coloring-matters.

The metallic elements that enter into consideration as possible constituents of the electrolyte are the elements usually present in lead bullion, those that may be in the fluosilicic acid as impurities at the start and the iron binding

## LEAD REFINING BY ELECTROLYSIS.

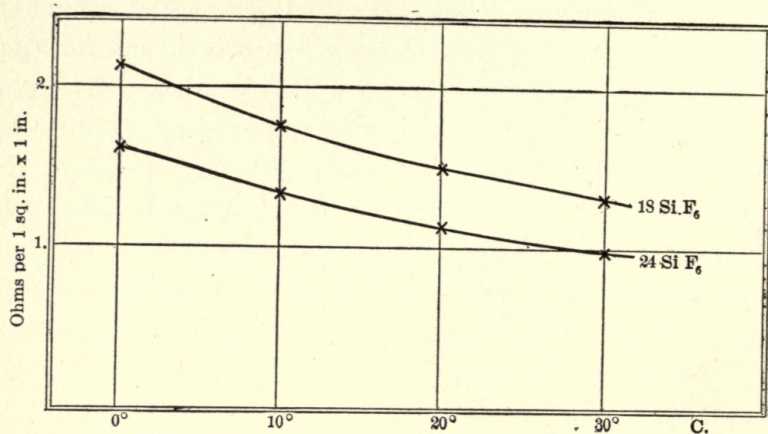


FIG. 3.

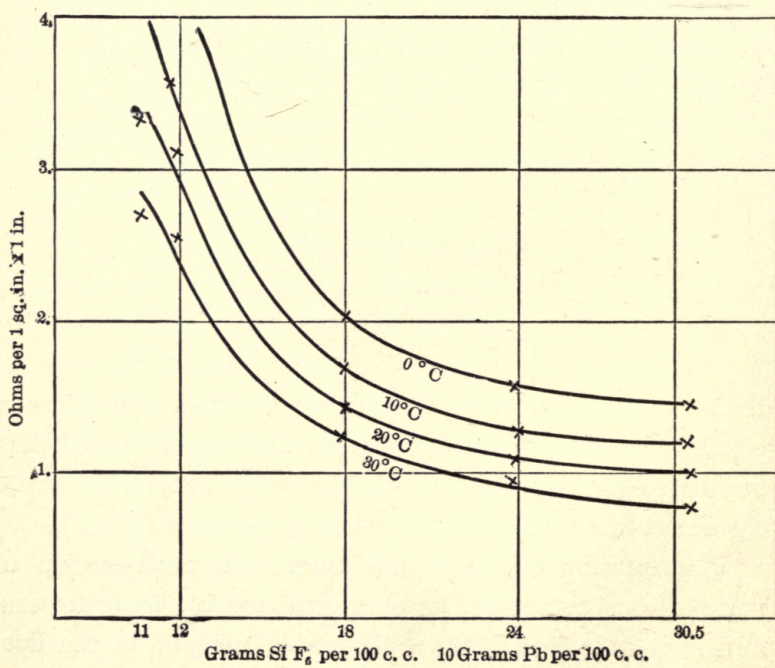


FIG. 4.



TABLE 18.

SiF <sub>6</sub> Grams per 100 cc.	Lead Grams per 100 cc.	Temperature.	Resistance.	Resistance at 20° C. Calculated.
23.3	23.6	19.5° C.	2.34	2.31
23.0	16	17. °C.	1.76	1.60
23.0	12	19. °C.	1.17	1.12
23.0	8	20. °C.	1.09	1.09
23.0	3.4	20. °C.	.87*	1.06
16.0	16.0	16. °C.	2.68	2.56
16.0	12.0	19.5° C.	2.07	2.05
16.0	8.0	20. °C.	1.49	1.49
16.0	4.0	20. °C.	1.31	1.31
12.0	12.0	15.5° C.	3.59	3.24
12.0	8.0	20. °C.	2.32	2.32
12.0	4.0	20. °C.	1.63	1.63
8.0	8.0	15. °C.	4.69	4.19
8.0	4.0	19. °C.	2.79	2.73
4.0	4.0	13. °C.†	9.22	8
63.0†	85.0	20. °C.	4.84	4.84

\* Incorrect. Correct figures is about 1.06.

† Saturated solution PbSiF<sub>6</sub>, specific gravity, 2.32.

TABLE 19.

SiF <sub>6</sub> Grams per 100 cc.	Lead Grams per 100 cc.	0° C.	10° C.	20° C.	30° C.
30.5	27.8	2.95	2.18	2.10	1.84
30.5	25	2.66	2.15	1.84	1.60
30.5	20	2.07	1.72	1.57	1.21
30.5	15	1.74	1.45	1.23	1.07
30.5	10	1.48	1.21	1.04	.75
27.1	25	3.22	2.49	2.13	1.86
24	20	2.73	2.24	1.72	1.52
24	15	2.01	1.67	1.33	1.14
24	10	1.62	1.33	1.14	.99
24	5	1.31	1.45	1.14	.87
21.9	20	3.39	2.68	2.32	1.99
18	15	3.50	2.99	2.34	2.09
18	10	2.13	1.77	1.50	1.31
16.4	15	3.80	3.25	2.54	2.28
12	10	4.62	3.74	3.35	2.69
11	10	4.84	4.13	3.51	2.81

of the tanks. The elements being considered then are iron, zinc, sulphur, copper, nickel, tin, antimony, arsenic, silver, bismuth, cadmium, gold, selenium, tellurium, and other elements in smaller quantities. Of these antimony, arsenic, silver, gold, copper, bismuth, selenium, tellurium are easily precipitable by lead, and consequently if they get into the solution they will be thrown out by the lead electrodes, mostly by the cathodes I believe, for the anodes are usually covered with slime, which would prevent their reducing, for instance, much antimony, although the antimony of the slime would quickly enough throw out such an easily precipitable metal as silver.

Zinc, iron, and nickel, if they find their way into solution remain there, as they are not precipitable by the lead electrodes, nor can they be in any way thrown out on the cathode by the electric current so long as there is a fair amount of lead in solution, which there always is. Analyses of lead bullion show the presence of iron and zinc in small quantities, say .02%. Whether the iron really does dissolve, I doubt, because the slime usually contains from one-half to two per cent of iron, accounting for at least a considerable part of it. The slime also contains sulphur as sulphides. As iron is not liberated in the lead smelting-furnace, but only iron sulphide, the lead then probably takes up small amounts of matte, and perhaps contains lead sulphide too.

It is difficult to see how any of the sulphur of the lead bullion could get into the solution, except possibly as  $H_2S$ . At any rate no sulphur has yet been either observed in the solution nor found in the lead by analysis.

The other element, tin, occupies practically the same position in the scale of electromotive forces of solution that lead

does. That is to say, it takes about the same electromotive force to deposit tin (from the acid solution) that it does lead, or to dissolve it from the anode. Consequently a mixture of tin and lead can behave as practically one metal.

Dr. Hans Mennicke\* made some researches on the refining of tin lead alloys, with a solution of tin fluosilicate. The solution was more difficult to prepare than the lead solution. No gelatine was added, but he produced good tin deposits so long as only a little or no lead was in the solution. With anodes of solder his deposits soon got spongy. With gelatine added, the deposits would probably have been solid. Both tin and lead dissolved from the anodes. Dr. Mennicke's results were not successful, but not conclusive either.

With about .02% tin in the anodes at Trail, some tin went over to the cathodes. After its presence, which was not suspected at first, was proved, it was removed by poling the lead before casting when the dross on the lead took up the tin. In such cases the dross could be smelted to lead containing tin, and the tin recovered by the usual softening process practiced as a preliminary in refining lead by the Parkes process. The percentage of tin found in the dross can be calculated on the basis that 4 or 5% of dross is produced. The analyses show:

Bullion.	Lead before Poling.
Average. . . . . .0289% Sn	Average. . . . . .0063% Sn

The analyses indicate that either part of the tin remains in the slime or part has already got into the dross before poling. The latter must have certainly taken place and probably the former to some extent too. In refining some bullion

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\* Elektrochemische Zeitschrift, Vol. XII, 112, 134, 161, 180.



with about 4% tin, very considerable quantities of tin remained in the slime. The tin in such slime dissolved out with evolution of hydrogen on treating with HCl.

A bar of fine solder (60 tin, 40 lead) I once made anode in a lead fluosilicate solution containing gelatine. The anode dissolved regularly and the cathode deposit was excellent. The experiment was not concluded.

Tin is very rarely found in lead bullion, but in case it is, part or all can be recovered from the dross produced in melting the cathodes, and the remainder in the slime can be recovered in several ways, if the quantity is large enough to make it pay.

*The nature and influence of the anode slime.*—Almost invariably in practical refining the anode slime remains attached to the anode, and very little change in appearance is noted, even when the lead is nearly all gone. This is especially the case when the lead contains a considerable amount of antimony, say 10%, when there is hardly any change in the color even. The slime is of varying degrees of hardness. The proportionate spaces occupied by the metal of the slime and the liquid with which it is saturated can be calculated with some accuracy. The data are: 1 cubic centimeter of lead weighs 11.36 grams, of antimony 6.7 grams, of copper 8.9 grams, and of silver 10.5 grams. Allowing 10% of lead in the slime, the actual space occupied by the slime from 11.36 grams of alloy (specific gravity practically the same as that of lead) is ordinarily about .035 cc., leaving .965 cc. for solution, or in percentages the solution occupies approximately 96–97% and the slime 3–4%. The metal of the slime is prevented from carrying any of the current passing through, at any rate after it has reached its final composition, by

polarization. To illustrate, suppose there is a piece of some metal lying below lead in the electromotive force series for fluosilicic acids, as copper, in the electrolyte between a lead anode and cathode, Fig. 5.

Instead of passing through the copper, by reason of its greater conductivity, the current passes around the copper on account of its polarization. Current can only pass to the

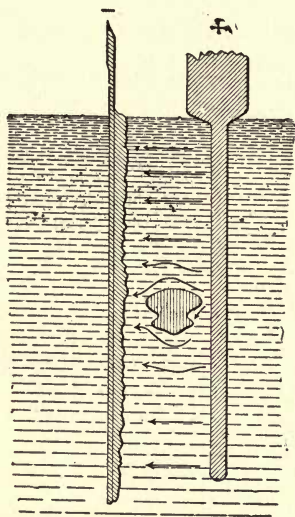


FIG. 5.

copper by depositing lead on it. On the other side where the current leaves, something else would have to dissolve, and this must be copper. To deposit lead on one side and dissolve copper from the other would require an electromotive force of about 0.5 volt. This is not the actual truth of the matter, because very small currents can pass to and from electrolytes and electrodes without any evidence of electrolysis. With more than an extremely small current the cur-

rent passes around the copper as if it were a piece of glass.

If now the current is increased so that the fall of potential in a distance about equal to the diameter of the copper piece approximates 0.5 volt, current will begin to go through the copper to a considerable extent, while copper goes into solution from one side.

The slime in practice consists of a number of different metals of course, antimony, arsenic, bismuth, copper, silver, and gold, with some combined lead. For the acid fluosilicate solution, the electromotive force series has been determined by dipping a piece of lead and of one of the other metals into the lead electrolyte, by Dr. Kern.

TABLE 20.

Pb.....	.0 volts.
Zn.....	+ .43 "
Al.....	+ .05 "
Sn.....	— .03 "
Fe.....	— .08 "
Sb.....	— .37 "
Bi.....	— .42 "
Cu.....	— .43 "
As.....	— .52 "
Ag.....	— .60 "
Pt.....	— .63 "
C.....	— .68 "

Such a method, however, cannot be accepted as giving the correct figures. A better way to determine these values is to prepare two fluosilicate solutions, one of the lead and one of the other metal, separate the solutions with a porous partition, dip the two metals in their respective solutions, and read the e.m.f. with a suitable instrument.

Somewhat different and more correct figures have been



obtained by placing lead fluosilicate solution both inside and outside of a porous cell, contained in a beaker. Such a cell as that shown in the sketch (Fig. 6) is useful and handy for such purposes.

It consists of a small piece of wood, which is heated in paraffine, and after cooling, pieces of paper, asbestos or cloth are cemented on the wood with warm paraffine. In this particular experiment I used ordinary cardboard as diaphragm.

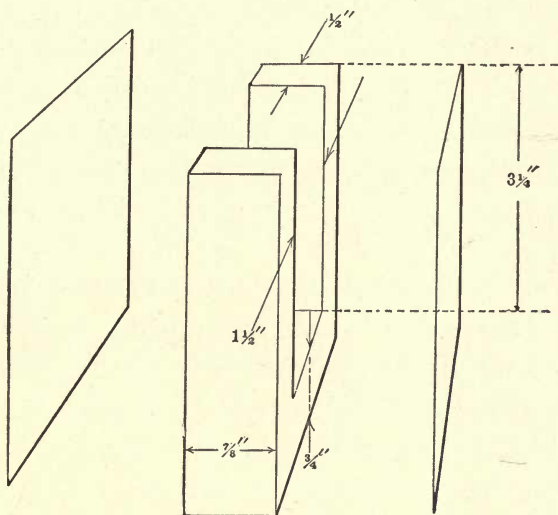


FIG. 6

A piece of the metal being tested is hung in the inside solution with a platinum wire and a piece of lead dips in the outside solution. A small current is passed for perhaps five minutes with the metal under investigation as anode. On shutting off the current the e.m.f. is read with a millivoltmeter. It is difficult to get a constant reading with arsenic, so I took the highest observed. I think the arsenious fluosilicate formed at first goes quickly over to arsenious acid, which gives a

lower e.m.f. against lead. As the mechanism of the reaction seems to be first the formation of an arsenious salt, the highest e.m.f. is the one with which we are concerned when investigating the possibility of arsenic dissolving with the lead. The series is given in Table 21.

TABLE 21.

Lead.....	.0	volts.
Arsenic.....	.40	"
Antimony.....	.43	"
Bismuth.....	.47	"
Copper.....	.51	"
Silver.....	.97	"

These figures represent an approximately correct series for most other oxygen-acid electrolytes. According to it each metal in the series cannot be precipitated by those preceding, while if the difference of e.m.f. is at all considerable (say 0.1 volt), each metal will precipitate those following. When the difference is, however, so small as between antimony and bismuth, no precipitation is usually observed to take place on dipping the higher metal into a solution of the next lower one. However, by the electrolysis of a mixed solution, for example, copper and bismuth methyl-sulphate, copper can be deposited out with little or no bismuth.

As we have seen already, with ordinary lead, such as contains say 3% of impurity, the space actually occupied by the metal of the adhering slime is only about 3% of the total. Under the conditions of electromotive force existing, this metal is practically non-conducting, on account of polarization. Its bulk is, however, too small to directly affect the conductivity of the solution with which it is saturated. It does have some small effect, however, by obstructing free circulation of the electrolyte in the neighborhood of the anode,

but the total resistance thus introduced is extremely small. In actual refining, there is rather a tendency for the electromotive force to fall off than to increase, as the electrolytic action on a set of anodes and cathodes goes on.

The usual thickness of an anode is about one inch, and the maximum thickness of slime then is about one-half inch. Any current so large or conductivity so low that the drop of potential in traversing one-half inch amounts to .4 volt, or .8 volt per inch, would be as capable of dissolving arsenic, antimony, bismuth, and copper from the surface layer, as of dissolving lead from the solid electrode beneath. With an electrolyte having a resistance for the cubic inch unit of 1.4 ohms, the maximum current strength per square foot permissible would be  $.8 \times \frac{1}{1.4} \times 144 = \text{about } 82 \text{ amperes}$ . As this is far beyond any current that it is practicable to use, there is never any danger of contamination of the solution or the refined lead from the direct attack of the anodes by the current, except in the case of tin. This statement applies only to lead alloys with a largely preponderating proportion of lead.

Regarding the nature and constitution of the slime, using as anode alloys of lead and various other metals, it makes some difference in the amount of lead retained by the slime what the other metal is, and how it is combined with the lead, and the speed of working appears to have some influence, high current density leaving more lead in the slime than low-current density. There appears to be no appreciable combination between copper and lead. Alloys of copper and lead have given a slime practically free from lead. Alloys with 40% copper and 60% lead can be treated easily. Experi-



ments were made by Dr. Kern, which are described in Chapter IX.

Silver also holds back very little lead. For example silver-lead alloys of composition given in Table 22.

TABLE 22.

Pb	88%	82.37%
Ag	9.75%	14.60%
Cu	1.53%	2.22%
Sb	.5%	.77%
Bi	1.11%	.19%

gave pure lead readily and slime containing only 1.5% Pb and 2.1% Pb, respectively. Very likely what little lead was left was in combination with the antimony and bismuth.

That lead does combine with some metals to form combinations not decomposed on electrolyzing the alloy as anode, is very forcibly brought out by Mr. Senn's experiment on the refining of lead-platinum alloy.\* The alloy contained 10.10% platinum, and the slime contained 70.45% Pb and .16% SiO<sub>2</sub>. In another experiment the alloy contained 10% platinum and left a slime of fine leafy crystals, containing SiO<sub>2</sub> 1.08%, Pb 65.30%, and Pt 32.93%, corresponding to the formula PtPb<sub>2</sub>. Even when the voltage was raised so high as 3 volts with oxygen evolution at the anode, the compound did not decompose to any great extent. Lead peroxide was formed, but that probably was deposited from the solution.

Bismuth probably retains about one-sixth of its weight of lead, and antimony  $\frac{1}{4}$  to  $\frac{1}{5}$  of its weight. The amounts can, however, be very different according to the current densities used.

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\* Senn, Zeitschrift für Elektrochemie, April 14, 1905.

The truth seems to be that the compounds of lead and other metals are decomposable, but only slowly. The slower the treatment the less lead in the slime. The maximum electromotive force available in practical refining for the decomposition of these compounds cannot well be over 0.05 volts on the average and 0.15 volts as a maximum, and probably some of the compounds with a small proportion of lead are able to resist this.

For the electrochemical decomposition of antimonides of lead, etc., the following experiment which I made is interesting: An anode of hard lead with about 18.8% antimony was used. Anode area 48 square inches.

TABLE 23.

Time.	Hours Run.	Current, Amperes.	Volts.	Current Density, Amperes per Square Foot.	Back E.M.F.
8.00	....	13		39	
8.30	....	10	.61	30	
10.30	2.5	10.5	.73	31.5	
11.30	3.5	10.5	.73	31.5	
1.30	5.5	10.5	.76	31.5	
3.10	5.5	10	.77	30	
4.00	6.3	9	.99	27	.232
4.45	7.0	8	.92	24	
5.00	7.5	5.5	.56	16.5	.232
9.30	24.0	1.5	.53	4.5	.304

The back e.m.f. was the voltage read with the voltmeter on interrupting the current, and is a measure of the chemical affinity of the antimony of the slime for more lead than it is already combined with. Analysis of the residue gave 7.83% lead.

The same anode was further electrolyzed with from 1 to 2 amperes, when the back e.m.f. finally rose to .328 volts,

and the residue became so fragile that it broke. The lead antimony compound was then nearly entirely decomposed. As the difference of e.m.f. of solution of lead and antimony is about .43 volts, the e.m.f. still falls short of that necessary to dissolve antimony.

The heat of combination of lead with excess of antimony is then about 17,000 cal.

Since the maximum voltage available in refining ordinary lead bullion for decomposition of antimonides is only about .10 to .15 volts, the antimonide of lead cannot be nearly completely decomposed in usual practice.

Pure lead was deposited by Dr. Kern in my laboratory from alloys of composition given in Table 24.

TABLE 24.

Pb.....	65.37%	65.56%	82.79%	88.52%
Bi.....	7.32%	6.94%	3.42%	2.28%
Sb.....	19.51%	18.24%	9.12%	6.08%
As.....	5.85%	5.47%	2.73%	1.82%
Ag.....	1.95%	1.94%	.97%	.68%
Cu.....	....	1.94%	.97%	.68%

It was necessary to work with a low-current density of about four amperes per square foot with the first two alloys, and use thin anodes, that would last say, six days, or what amounts to the same thing, clean them every six days. The slime from the first two alloys contained 5.30% Pb beside the bismuth, silver, copper, antimony, and arsenic. With the second two alloys, a continuous run was made without cleaning anodes of ten days, back e.m.f. at end—.07 volts.

For an idea of the amounts of lead held back by antimony, copper, and bismuth, the table from Mr. Senn's paper is instructive.



TABLE 25.

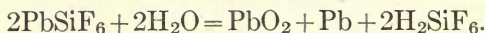
No.	Anode Contains	Amperes.	Current Amperes, Sq. Dm.	Amperes, Sq. Ft.	Dura- tion, Hours.	Lead De- posited, Grams.	Quantity Slime, W.	Deposited Lead Contains
27	.92% Cu	.5	.59	5.7	29	55.9	1.64	No Cu
28	.92% Cu	.9	1.07	10.2	24	83.3	.87	No Cu
29	1.006% Cu	1.3	1.55	14.9	18	90.2	3.11	No Cu
30	1.006% Cu	2	2.30	20.2	9	69.4	1.10	No Cu
31	12% Bi	.5	.59	5.7	24	48.3	.....	No Bi
32	12% Bi	.9	1.07	10.2	7.25	25	12.72	No Bi
33	12% Bi	1.3	1.55	14.9	11	55.1	12.60	No Bi
34	26.67% Bi	.9	1.07	10.2	17	59.	13.25	No Bi
35	26.67% Bi	1.3	1.55	14.9	16.5	82.6	36.38	.94% Bi
36	10.03% Sb	.5	.59	5.7	30	57.9	8.58	No Sb
37	10.03% Sb	.9	1.07	10.2	8.5	29.5	5.19	No Sb
38	10.03% Sb	1.3	1.55	14.9	2	110.3	18.52	.13% Sb
39	9.81% Sb	1.3	1.55	14.9	18	90.3	10.43	.05% Sb
45	10.01% Pt	.28	.59	5.7	16			

No.	Analysis of Slime.						Solution.
	Pb %	Cu %	Bi %	Sb %	SiO <sub>2</sub> %	F %	
27	.....	23.41					9% Pb—11% free
28	.....	36.31	.....	.....	28.47		H <sub>2</sub> SiF <sub>6</sub> falling to
29	.....	19.47					4.83% Pb—8.56%
30	10.03	57.96	.....	.....	25.12		free acid.
31	.....		70.49				
32	.....		42.46				
33	.....		35.44				
34	12.4		83.97	.....	1.82		
35	34.83		60.15		1.26		
36	.....			67.71	.....	.9	9% Pb—11% free acid
37	.....			47.52	1.04		falling to 2.48% Pb—
38	.....			53.47			11.5% free acid.
39	.....			45.00			
45	.....	.....	.....	.....	.....	.....	

The actual amount of lead thus retained with anodes of ordinary grades of lead bullion is quite small. If 60 pounds of slime are produced per ton of lead, and it contains 12% lead, which is a fair average, the amount of lead in the slime is 7.2 lbs. = 0.37% of the total.

The electrolysis of the fluosilicate solution with an insol-

uble anode is interesting. In this case lead deposits on the cathode and lead peroxide on the anode leaving fluosilicic acid.



This reaction may be useful, for instance if it becomes necessary to reduce the percentage of lead in the solution for any reason. Storage batteries have been constructed to work on this principle, but there are mechanical difficulties which have yet to be overcome. If a purification of refining solution became necessary the lead could be removed in this way and the solution distilled or purified in other ways.

From the analogy to electrolytic copper refining the question of purifying the electrolyte was early given a good deal of consideration, and a number of purifying schemes proposed. We now know that the question of purification of solutions will never come up in refining ordinary grades of bullion. The only metals of the anodes that can accumulate in the electrolyte are iron, zinc, nickel, and cobalt. Most of the iron, which is very small in amount, remains in the slime and the others are only present in traces. The total amount of these metals dissolved is probably not over .01%. The loss of electrolyte, which will be .3 cubic foot or more per ton lead refined, permits a maximum of iron, etc., assuming .01% to dissolve of at most 1.07% of these metals in the solution, which is too small to be serious.

As the preparation of pure lead may be of interest, the following quotation from a paper by Dr. Kern and myself on the "Lead Voltameter,"\* is given:

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\* Trans. Am. Electrochemical Society, Vol. VI, page 67.

"The solution was diluted so as to contain 17 grams of  $\text{PbSiF}_6$  and 7 grams of free  $\text{H}_2\text{SiF}_6$  in 100 cc. solution. After adding one gram of gelatine (dissolved in hot water) to 2000 cubic centimeters of solution, the electrolyte was rendered absolutely pure, in respect to metals which can deposit with lead, by electrolyzing for several days, using electrodes of refined lead. The anodes were wrapped with two thicknesses of clean linen, so as to prevent the impurities from dropping off and floating in the electrolyte. The small amount of soluble impurities in the electrolyte was due principally to the impurities in the white lead used for making the solution. The electrolysis was continued for four days at temperatures between  $17^\circ \text{C.}$  and  $57^\circ \text{C.}$ , using a current density at the electrodes of 10 to 12 amperes per square foot. A small amount of 'anode sludge' remained behind, and in order to prevent it from being oxidized by the atmosphere and subsequently going into solution, melted vaseline was poured on the surface of the electrolyte. The deposit which formed on the cathode was smooth, dense, and non-crystalline.

"After purifying the electrolyte, about 800 grams of absolutely pure lead was made by electrolysis, using ordinary refined lead, wrapped with clean linen, for the anodes. The refined lead which was deposited on the cathode was further refined by reversing the current density and re-depositing it on new cathodes. The solution was protected from the atmosphere by a covering of melted vaseline. The purified lead was melted, cast into a thin plate, and then rolled into sheets about  $\frac{1}{32}$  inch to  $\frac{1}{16}$  inch thick. The sheets were cut into strips of suitable size and used as anodes for the lead voltameter. No residue was left on dissolving the purified anodes by electrolysis."



## CHAPTER II.

### CHEMISTRY OF SLIME TREATMENT.

LEAD slime contains originally metallic lead, copper, gold, silver, bismuth, antimony, arsenic, sulphur, and occasionally probably other elements, tin, selenium, and tellurium. For analyses see Table 26. The object of its refining is to recover especially the gold and silver, but the bismuth, antimony, copper, and lead are also valuable and should be saved.

There are several different methods of treatment, based on different chemical or physical properties of the various metals.

These methods are distillation, amalgamation, fusion to alloy, followed by chemical or electrochemical treatment of the alloy, fusion to bullion and slag, fusion to matte and slag, electrolytic refining of the slime direct, dry treatment with chlorine and separation of the chlorides by distillation, and various wet chemical and electrochemical methods of treatment.

**Distillation.**—The temperatures necessary to distil the metals could easily be obtained in an electric furnace, and nothing would be simpler than to separate the metals in this way, apparently. The energy requirement would not be large. The trouble is that the boiling-points of the three principal metals, lead, antimony, and silver, lie too close together. That antimony boiled as high as 1600°, as deter-

TABLE 26.

## SLIME ANALYSIS.

No.	Anodes.	Cu, Per Ct.	Ag, Per Ct.	Sb, Per Ct.	As, Per Ct.	Pb, Per Ct.	Bi, Per Ct.	S, Per Ct.	Fe, Per Ct.	Oz. Au, Per Ct.	Se, Per Ct.	Te, Per Ct.	
1	Lead, Trail, B. C.	8.83	28.15	27.10	12.42	17.05	nil	.....	1.27	.....	.....	.....	Trans. Am. Inst. Min. Eng., 1904, p. 182.
2	Lead, Trail, B. C.	22.36	23.05	21.16	5.40	10.62	nil	.....	1.12	.....	.....	.....	Trans. Am. Inst. Min. Eng., 1904, p. 183.
3	Lead, Monterey, Mex.	1.90	32.11	29.51	9.14	9.05	trace	.....	.49	29.1	.....	.....	Original. Mines and Minerals, Vol. 25 (1905), p. 288.
4	Lead, Mexican.	9.30	4.7	25.32	44.58	10.30	.52	.....	nil	.....	.....	.....	Original. Mines and Minerals, Vol. 25 (1905), p. 288.
5	Lead, Mexican.	6.38	3.90	50.16	15.23	5.30	19.74	nil	.....	180.33	.....	.....	Original. Mines and Minerals, Vol. 25 (1905), p. 288.
6	Lead, Trail, B. C.	1.40	31.62	35.71	4.91	9.57	.....	.....	.....	81.99	.....	.....	Original. Mines and Minerals, Vol. 25 (1905), p. 288.
7	Lead, Trail, B. C.	6.60	32.21	24.60	2.20	12.60	.....	.....	.....	.....	.....	.....	Original. Mines and Minerals, Vol. 25 (1905), p. 288.
8	Rich Lead, Parke's Process.	12.56	78.45	4.12	.....	3.00	.88	.....	.....	.....	.....	.....	Original. Mines and Minerals, Vol. 25 (1905), p. 288.
9	Lead, Trail, B. C.	7.10	29.20	30.50	6.10	10.20	.....	.....	.....	.....	.....	.....	Original. Mines and Minerals, Vol. 25 (1905), p. 288.
10	Lead, Trail, B. C.	7.70	31.90	37.60	2.80	12.60	.....	.....	.....	.....	.....	.....	Original. Mines and Minerals, Vol. 25 (1905), p. 288.
11	Lead from El Doctor Mine, Mex.	7.82	2.44	75.34	0.24	12.23	1.95	.....	.....	.....	.....	.....	Original. Private Comm. Private Comm.
12	Lead, Trail, B. C.	9.50	17.10	25.91	5.96	14.50	.....	.....	.....	34.50	.....	.....	Original. Private Comm. Private Comm.
13	Lead, Chrome, N. J.	5.47	21.94	32.67	0.51	9.43	9.71	.....	.....	.....	trace	.59	Original. Private Comm. Private Comm.
14	Copper, Montana Converter Anodes.	41.	24.	.....	.....	.....	.....	.....	.....	18.	.....	.....	Trans. Am. Inst. Min. Eng., 1904, p. 310.
15	Copper, Montana Reverbatory Anodes.	18.	51.4	.....	.....	.....	.....	.....	.....	38.	.....	.....	Trans. Am. Inst. Min. Eng., 1904, p. 310.
16	Copper, Boston and Montana.	57.	14.80	2.00	2.60	5.26	5.70	.....	.....	.....	2.0	1.0	Original.
17	Copper, Boston and Montana.	53.29	12.90	3.30	1.15	trace	1.55	11.96	.....	.....	.26	1.97	Original.

mined by V. Meyer, did seem surprising, as antimony is regarded in smelting as a volatile element. Its volatility in smelting is due to the low boiling-point of its oxide, however. I was unable to volatilize any antimony on heating it in a carbon crucible in an anthracite fire, and the temperature was certainly high enough to melt steel.

Messrs. Moissan and Watanabe\* report the results of experiments on the distillation of alloys of nearly equal parts copper and silver; and of tin 64% and silver 35%, and of lead 53% and silver 46%. The alloys were heated for various periods in an electric furnace and the residual metals weighed and analyzed. I have plotted the results as Figs. 7, 8, and 9. The last two figures are based on only three determinations each, and the curves are in consequence not necessarily entirely correct in form. They show no complete separation of metals by distillation.

**Amalgamation.**—Lead, copper, gold, silver, and bismuth amalgamate easily, and arsenic and antimony do not, so that a separation might be made. Fresh unoxidized slime has been ground with mercury and some fluosilicate electrolyte in a mortar, and the mercury takes up a portion of the silver, gold, copper, and lead, but the separation is very far from complete, probably because the metallic arsenides, antimonides, and other compounds present in the slime are too stable to be decomposable by mercury. Even after the separation was made by amalgamation, considerable still remains to be done before the metals are finally recovered. The bullion could be retorted as it is usually done in amalgamation silver mills, or an electrolytic method for extracting silver,

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\* Comptes Rendus 1, CXLIV, 1907. Number 11, page 16.



copper, lead, and bismuth from the amalgam might be devised.

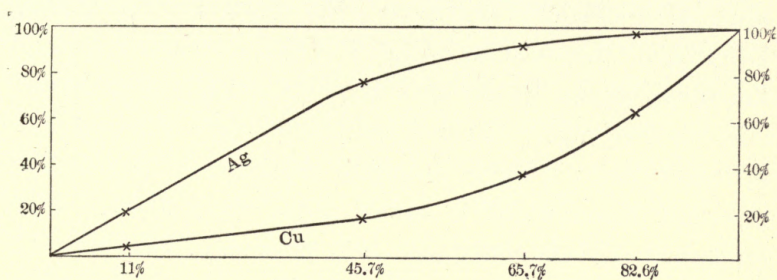


FIG. 7.

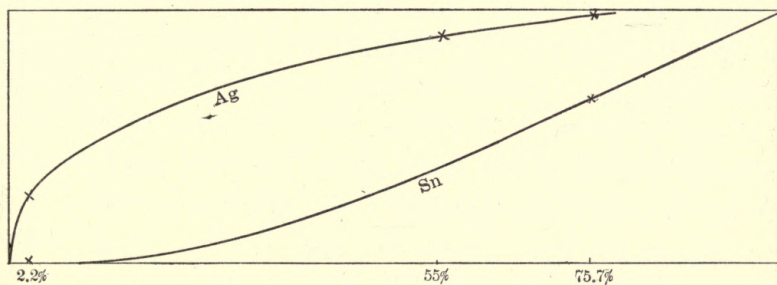


FIG. 8.

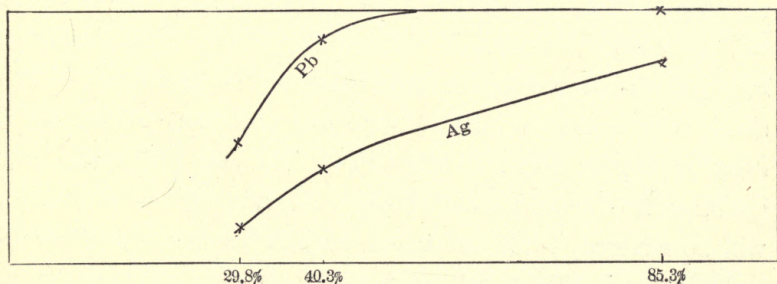


FIG. 9.

**Fusion to alloys.**—Slime oxidizes rather readily when dry, and some varieties will inflame spontaneously on drying,

so that to melt it without oxidation one has to be careful. A good way to do, experimentally, is to put the still moist slime in a crucible, and cover the crucible while melting. Even then, the escaping steam is liable to oxidize some of the slime, especially the antimony. Whether steam actually does oxidize finely divided antimony with production of hydrogen, has not been definitely determined. Some slime, especially slime which is rather dense, from anodes rather lower in lead, containing say 10% antimony, melts with the formation of little or no slag to a clean alloy.

As lead is rather objectionable in alloys that are to be treated with solutions containing sulphuric or hydrofluoric acids, on account of the insoluble lead sulphate or fluoride that forms, it is desirable to get the lead out as a slag in melting, if possible. This may be done quite readily with slime from ordinary bullion by mixing the fresh slime, pressed as dry as possible on the filter, with enough concentrated HCl to convert the lead present into lead chloride. If the slime contains say 12% of lead, about 12% by weight of 40% HCl is right. Some reducing agent, as flour, may also be added advantageously. On melting the moist mixture in a crucible an alloy is produced containing silver, gold, bismuth, some of the copper and a large part of the antimony of the slime, with a slag of lead chloride and antimony oxide, and a scum of copper and lead sulphides. The slag and scum may go back to the lead blast-furnace of course, where its values will be covered, while the metal may be electrically or chemically refined. This melting method on one occasion failed, and the hydrochloric acid escaped, no lead chloride or other slag being formed. The slime was a heavy one from lead containing much antimony.

As an example, a light slime containing bismuth was washed and a moisture determination made to get the dry weight, which was found to be 300 gr. One hundred grams lead chloride and about 30 cc. concentrated HCl, and a few grams tartaric acid as reducing agent were added and the whole stirred together. The mixture was added in portions to a small crucible and heated to a red heat. A good deal of smoke from burning tartaric acid and arsenic came off. The products were 135 grams of metal and about 140 of slag, and some additional slag was absorbed by the crucible. About 20 grams of scum, that looked like galena, remained in the crucible.

On analysis the slag was found to contain 9% antimony, 1% iron, trace of bismuth and arsenic, and 1% copper, the remainder being mostly lead chloride. The metal contained 30.2% silver, a trace of lead, 2.5% copper, and 13.0% bismuth. The remainder was mostly antimony, not determined however.

In another experiment, 224 grams slime (dry weight) melted with HCl, but without lead chloride, gave 82 grams metal and 75 grams of slag.

A complete separation of lead is thus obtained, while all the bismuth goes into the metal as well as about 80% of the antimony.

Fused lead chloride makes an excellent electrolyte for depositing metals, so the slag was electrolyzed with carbon electrodes at a red heat.

There are present  $\text{Sb}_2\text{O}_3$  and  $\text{PbCl}_2$ . As the reaction,  $\text{Sb}_2\text{O}_3 + 3\text{PbCl}_2 = 2\text{SbCl}_3 + 3\text{PbO}$  can only take place with loss of energy, it need not be considered to occur. The heats of formation of these compound are:



$$\text{Sb}_2\text{O}_3 = 166,900 \text{ cal.}$$

$$3\text{PbCl}_2 = 251,700 \text{ “}$$

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$$418,600 \text{ “}$$

$$2\text{SbCl}_3 = 182,800 \text{ cal.}$$

$$3\text{PbO} = 152,400 \text{ “}$$

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$$335,200 \text{ “}$$

Therefore reduction by carbon ought to yield metallic antimony in preference to lead as the reaction,  $\text{Sb}_2\text{O}_3 + 3\text{C} = 2\text{Sb} + 3\text{CO}$  requires 79,420 cals., and the reaction  $\text{Sb}_2\text{O}_3 + 3\text{C} + 3\text{PbCl}_2 = 3\text{Pb} + 2\text{SbCl}_3 + 3\text{CO}$  requires more, namely, 146,320 cals.

Reduction by carbon could only take place at a rather elevated temperature, as the reactions are strongly endothermic at low temperatures, and the volatility of both lead chloride and antimony trioxide is too great at high temperatures. Electrolytic reduction of the slag with carbon anode, which carries out the same reactions, and carbon cathode was tried with some success, and 18 grams of metal reduced with high current efficiency, containing: silver 14.5%, copper 4.7%, lead 39.0%, antimony 40.0%.

The presence of all this silver indicates that there were either metal shot in the slag to start with, or some silver was reduced from the scum. The quantity of silver in this product was relatively small, about 5.85% of the total accounted for. Probably the heat in the original melting was not high enough to thoroughly melt the slag. The temperature was only a red heat.

The treatment of the alloy and similar artificial alloys was attempted by various methods, dry and wet.

For treatment with chlorine we consider the heat of combination of the various metals present, with chlorine, the figures being as follows:

TABLE 27.

$\frac{1}{2}$ PbCl <sub>2</sub> .....	41,950 cal.
CuCl.....	35,400 "
$\frac{1}{3}$ SbCl <sub>3</sub> .....	30,467 "
$\frac{1}{3}$ BiCl <sub>3</sub> .....	30,233 "
AgCl.....	29,000 "

Bismuth is capable of forming a bismuth bichloride, of which the heat of formation is probably somewhat greater. Chlorine would then apparently take out the copper, and then the bismuth. On passing chlorine into the metal in a crucible much volatile SbCl<sub>3</sub> came off at once, which was not desired or expected.

The heat of formation of cupric chloride from cuprous chloride ( $\text{CuCl} + \text{Cl} = \text{CuCl}_2$ ) is 16,000 cals., and it would accordingly act on the alloy as a chloridizing agent. Experimentally it could be applied more conveniently and in better regulated amount than chlorine. I accordingly melted together an alloy of this composition:

Antimony.....	65.2%
Copper. ....	13.2%
Bismuth.....	21.6%

This was put in a porcelain crucible with some PbCl<sub>2</sub> and NaCl for a cover, and 55.5% of anhydrous CuCl<sub>2</sub> by weight added, or enough to chloridize the copper of the alloy to CuCl and the bismuth to BiCl<sub>2</sub>.

No such reactions took place. Antimony chloride came off in large quantity. The resulting alloy contained 31.5%



copper and the slag 38%. The metal also contained 19–20% bismuth.

In general it has been found that precipitation of one metal by another from a fused melt is greatly influenced by the formation of compounds among the metals of the alloy themselves, and that the reactions are rarely complete and do not always proceed as indicated by the formation—heat figures.

**Dry chlorination of slime.**—The metals can, however, be separated by converting them into chlorides and fractionally distilling the chlorides.

TABLE 28.

Arsenic	chloride	AsCl <sub>3</sub>	boils at	134° C.
Antimony	"	SbCl <sub>3</sub>	" "	223° C.
Bismuth	"	BiCl <sub>3</sub>	" "	435° C.
Copper	"	CuCl	" "	1000° C.
Lead	"	PbCl <sub>2</sub>	" "	white heat.

For conversion into chlorides there is, of course, no necessity of first melting to an alloy, as the chlorine may be passed into the slime.

In one experiment 250 grams of slime, containing about

Copper.....	12.5%
Bismuth.....	20. %
Arsenic.....	15.7%
Antimony.....	11.3%
Silver.....	18.3%
Lead.....	10 %

was treated in a flask with chlorine. 133 grams of chloride distilled over, but the chlorine did not penetrate the mixture thoroughly. There is no difficulty about removing



arsenic and antimony as chlorides, in this way, leaving lead, copper, and bismuth chlorides in the residue, and also in distilling off the bismuth if desired.

The heat generated by the reaction of cold chlorine on cold arsenic, for example, is sufficient to vaporize it and raise it to a very high temperature, but the thermochemical data to determine this temperature are not at hand. The reaction on the other metals is just as violent, so that on operations of any magnitude no external heating is necessary to drive off the arsenic, antimony and bismuth, and probably the temperature would go beyond the boiling-points of lead and copper chlorides, leaving silver and gold bullion in the melted state, with some slag of copper chloride, if the right amount of chlorine was used. This is not an entire innovation, for the treatment of gold with chlorine for removing silver and base metals has been successfully carried out for years, the process having been originated by Mr. F. B. Miller of the Sydney Mint, in 1867.\* Clay crucibles are stated to be used, rendered impenetrable to the silver chloride by dipping them in hot concentrated borax solution before using.

The chlorine for treating slime could be readily made by electrolyzing fused lead chloride, which is one of the easiest, if not the easiest, of all fused salts, to decompose electrolytically. It has never been done commercially because lead chloride is not a raw material, but in the chlorination of slime the chlorides of copper, silver, antimony, and bismuth produced are reducible by lead, giving the metals and lead chloride.

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\* Rose's Metallurgy of Gold, page 441. Eissler's Metallurgy of Gold, page 615.

A difficulty is the storage of chlorine. The electrolytic plant should run continuously and the chlorine would be required intermittently. This has probably been one of the reasons why chlorination has not been applied more in metallurgy. It seems to me that an easy way to store chlorine is to condense it by means of sulphur to sulphur chloride, and produce chlorine therefrom by warming the sulphur chloride. At temperatures below  $30^{\circ}\text{C}$ . the mixture saturated with chlorine has the composition  $\text{SCl}_4$ . At  $6^{\circ}$  the composition is  $\text{SCl}_2$ , and at  $139^{\circ}$   $\text{SCl}$ . Chlorine is very readily absorbed by the sulphur and its chlorides at the appropriate temperatures. In a paper on his chlorine smelting process Ashcroft\* has described methods of pumping and drying chlorine. A special process for drying chlorine is not necessary in presence of sulphur, as sulphur chlorides decompose water. The chlorine vaporized from sulphur chloride will contain some sulphur, but this is a desirable circumstance, as any metallic oxides are readily converted to chlorides by sulphur chloride, even such oxides as those of aluminum and silicon being convertible in this way.†

The conversion of the chlorides of antimony and bismuth into metal is easy in the case of bismuth, because all that it is necessary to do is to decompose the bismuth chloride with melted lead. Antimony chloride boils below the melting-point of lead and well below the melting-point of antimony, so that it would have to be passed into melted lead as a vapor.

It has been proposed† to treat slime with chlorine in the

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\* Electrochem. and Metall. Industry, Vol. IV, 1906, page 96.

† U. S. patent, Betts, 712640, November 4, 1902.

presence of water, producing a solution containing antimony, arsenic, and bismuth trichlorides, and a precipitate of lead chloride and cuprous chloride, insufficient chlorine being used to chlorinate the silver and gold (which is possible on account of the lower combining heat of silver, and especially of gold for chlorine), filtering, boiling off arsenic and antimony chlorides and water, and taking up the residue with water to remove lead chloride. The distillation of antimony chloride solution is not as satisfactory as might be believed from reading descriptions of it, because it decomposes into oxide and hydrochloric acid, unless a large excess of HCl is used. It would be difficult to find materials for carrying out the distillation on a large scale. The dry chlorination is then much superior, in which case the heat of reaction will be sufficient for the distillation, so that the apparatus question is not a difficult one at all in that case.

**Direct fusion with soda.**—Most slime, and slime from ordinary grades of bullion, if dried and warmed, is very apt to oxidize so rapidly as to sinter or turn yellow, according to its composition. The oxidation takes place in two stages; one is a slow oxidation at a low temperature, the product being black and soft. If the temperature is high enough, the slime oxidizes rapidly, and if it contains considerable antimony, say 40 or 50%, it is not so apt to sinter, but yields a yellow product. This is mainly antimony pentoxide, and it is a difficult material to treat. It is insoluble in acids and infusible. It fluxes with soda, but only at a high temperature. Heated with powdered charcoal, however, it may be reduced to the very easily fusible trioxide. The same end may be accomplished by heating it with raw, unoxidized slime.



At Trail the slime contains about 30% antimony, 20% silver, 10% copper, 6% arsenic, 10% lead, beside gold.

The process worked out by the Canadian Smelting Works and in use there still has been described as follows: It was originally intended to boil the slime with sodium hydrate and carbonate to dissolve out the antimony,\* oxidation being performed by drawing a current of air through the solution and melting the remainder in a magnesia-lined reverberatory to a doré bullion. The antimony failed to dissolve in more than very small quantities, so this step was omitted from the process, and the slime melted directly. Copper is difficult to remove in this way, and this was got around to some extent by skimming all the dross possible from the lead before making anodes.

The slime is placed in iron wheelbarrows or trucks and wheeled into a large brick oven, with thin walls, which can be heated evenly with coal fired outside. After the slime is pretty well dried, it is dumped into a brick stall, where there is a good draught, when it ignites and roasts, copious fumes of arsenic coming off. After oxidizing it is melted down in a reverberatory with soda to a doré bullion. The slag averages about 30–40% Sb, 5–8% Cu, 10–15% Pb, with considerable silica, and from 200 to 600 ozs. of silver per ton. The Trail refinery is using this process temporarily, until they have completed their experiments to devise a better process. To get the right amount of oxidation, which varies with unavoidable variations in composition and roasting of the slime, either coal dust or nitre, as the case may be, is added to the melt in the furnace. The melting part of the

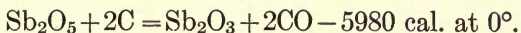
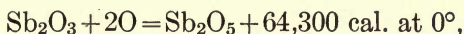
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\* Mines and Minerals, Vol. 25 (1905), page 28.

process is not satisfactory on account of the high temperature and metal losses, nor are by-products (except copper) recovered in marketable form.

In this process the antimony is probably slagged off partly as  $\text{Sb}_2\text{O}_5$  combined with some soda, and as  $\text{Sb}_2\text{O}_3$ .

**Melting without fluxes, slagging antimony as  $\text{Sb}_2\text{O}_3$ .—**Antimony trioxide melts below a red heat, but contact with air or oxidizing gases makes the melted trioxide soon get pasty and finally infusible. This is because the reaction  $\text{Sb}_2\text{O}_3 + 2\text{O} = \text{Sb}_2\text{O}_5$  is quite vigorous. If powdered coal or ground antimony be stirred in the product, another reaction takes place, and the easily fusible trioxide results again.



At  $700^\circ$  the latter reaction is still slightly endothermic, but it occurs readily enough. Perhaps some of the reduction, in the case of carbon, is done by the CO produced, with evolution of heat. Unoxidized slime will perform the reduction as well.

By melting slime which is only partially oxidized, or proper mixtures of thoroughly oxidized and unoxidized slime, and keeping any excess of oxidizing gases carefully away during the melting, a black, glassy, and extremely fusible slag results, and a metallic product containing the silver and variable amounts of lead, antimony, and copper, according to the proportion of oxygen present. As slime contains usually sulphur, a matte containing 20–30% silver and about 50% copper is also produced, if there is not too much oxygen

present. The difficulties are in getting just the right proportion of oxygen and loss of antimony trioxide by volatilization. At the temperature necessary to melt the silver antimony trioxide volatilizes very fast. If some antimony and lead are left in the silver by deficiency of oxygen, the temperature may be much reduced, but the metal requires another treatment to remove antimony and lead. If the melt is not well covered, the pentoxide will form, so that a reverberatory furnace is not suitable, both for this reason and on account of the volatilization difficulty. No satisfactory crucible has been found, as the slag attacks most crucibles rapidly. My experiments indicate, however, that a cast-iron crucible will do quite well. The electric furnace is the remaining means, and is entirely feasible from a power standpoint and admits of melting large quantities rapidly with little loss. The specific heat of slime can be roughly calculated as follows:

TABLE 29.

Heat in melted silver	at 960° per lb.	89.15 lb. cal.
Heat in $\text{Sb}_2\text{O}_3$	" 960° " "	200 " "
Heat in $\text{Pb O}$	" 960° " "	150 " "
Heat in $\text{Cu}_2\text{S}$	" 960° " "	200 " "
Volatilization $\text{AS}_2\text{O}_3$	" 960° " "	200 " "
Heating and vaporizing $\text{H}_2\text{O}$	" 960° " "	700 " "

These are the principal constituents. The figures are not known for antimony, lead, and arsenic oxides, and can only be very roughly got from comparison with compounds for which the exact figures are known. The above figures will do for our present purpose, as will be readily seen below.

Suppose the slime contains



TABLE 30.

H <sub>2</sub> O	15%	= 102.5	lb. cal.
Silver	30%	= 27.0	"
Sb <sub>2</sub> O <sub>3</sub>	30%	= 60.0	"
As <sub>2</sub> O <sub>3</sub>	10%	= 20.0	"
PbO	10%	= 15.0	"
Cu <sub>2</sub> S	5%	= 10	"

Heat required in lb. cal.    234.5

(The pound calorie is the amount of heat required to heat one pound of water, one degree centigrade, and is equivalent to .00052 K.W. hours, or .00069 E.H.P. hours, in electric energy.)

The heat necessary at 100% efficiency per pound of slime is 0.12 K.W. hours; at 50% efficiency, which is easily obtained, and for lead producing 80 lbs. of slime per ton, 20 K.W. hours would be necessary for melting. This is so small that quite large proportionate errors in the specific heats above would not make any practical difference.

Not all types of electric furnace would be suitable. Contact with hot carbon would tend to reduce the slag and render the precipitated metal too base. A furnace heated by radiation from an arc or a heated carbon rod would do, but a furnace of the resistance type, in which the heat is generated in a narrow conductor of the metal, would seem to be best adapted. The heating current may either be induced as in the Colby or Kjellin\* and similar furnaces. That electric furnaces will be used in slime and silver melting is probable. Small induction furnaces for melting steel and

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\* Colby, U. S. patents 428378 and 428379, May 20, 1890; Gin., 771872, Oct. 11, 1904; Schneider, 761920, June 7, 1904; Betts, U. S. Patent 816558, April 3, 1905.

brass are now on the market and in successful use,\* but the material of which the crucibles are made would have to be changed for slime melting, and some arrangement would be necessary to catch the fumes given off.

When the slime contains bismuth in appreciable quantity the melting process is at its best, because the bismuth is intermediate in oxidizability between silver on the one hand, and lead and antimony on the other, and as a consequence the percentage of oxidation does not need to be so carefully controlled to insure a separation of gold and silver from lead and antimony. In case the oxygen is higher than usual, more bismuth is slagged; in case the oxygen is lower, more bismuth goes into the doré, while in either case the antimony and lead remain almost entirely in the slag, and the silver as metal. Also the presence of bismuth in the silver increases its fusibility, so that the melting temperature need not be nearly so high. The slag high in  $\text{Sb}_2\text{O}_3$  is so fusible that it melts below a red heat.

These facts are brought out well from the analysis of the products resulting from the melting down of some partially air-oxidized slime in my laboratory.

TABLE 31.

	Metal 35 Gr.	Slag 80 Gr.	Matte about 2 Gr.
Au. ....	.78%		
Ag. ....	66.23%		
Bi. ....	20.3%	2.95%	30%
Cu. ....	5.1%	1.15%	46.3%
Sb. ....	1.3%	28%	None.
Pb. ....	.8%	34.9%	None.

The value, 5% for copper in metal, is probably too high, as the sample may have contained a little intermixed matte.

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\* Electrochemical and Metallurgical Industry, 232, 1907.

On cooling the bar bismuth liquates out in little drops that can be knocked off. These contained little beside bismuth. The analysis showed 87% bismuth, 6% silver.

The treatment of these products can be carried out successfully. The bullion may be parted by the methyl-sulphate method, as described in Chapter IV, and the slag may be freed from bismuth, if required, by melting it with a little antimony. The residual slag yields its antimony to hydrofluoric acid, from which solution it may be deposited electrolytically as described in Chapter III. About one-half the copper present also dissolves in the HF, the removal of which will be taken up with the description of antimony depositing.

Dilute nitric acid was tried for dissolving lead and bismuth from the slag, after which the residue could be converted into antimony or antimony compounds. If the nitric acid is not very strong little or none of the antimony is converted to higher oxides, as it is difficult to peroxidize it. Nitric acid acts slowly on the slag, finally leaving a soft light yellow, rather dense residue of antimony oxide and a solution of lead nitrate, which can be easily crystallized.

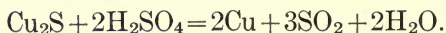
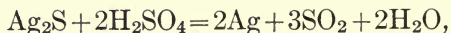
Mattes high in silver are analogous to the sulphides made from silver ores in a hyposulphite leaching mill. There are several methods for treating such material. Stetefeldt's process of melting the sulphides in an iron pot, roasting, and dissolving out copper sulphate with water in presence of metallic copper to precipitate any silver in solution, would seem to be applicable to the present material from the roasting stage on. The residue from the copper extraction consists mainly of silver. The roasting was, as described by Stetefeldt, performed in a small muffle-furnace after being first ground in a small ball-mill. Details will be found in



Stetefeldt's, "The Lixiviation of Silver Ores with Hyposulphite Solutions," and Collins' "Metallurgy of Silver."

The sulphuric acid process (Dewey-Walter process) consists in boiling the sulphides with hot concentrated sulphuric acid in an iron pot. The sulphuric acid oxidizes the sulphur of the sulphides as well as the metals. It seems reasonable to suppose that the matte, if ground fine, would react similarly to precipitated sulphides. If so, this method would be much simpler and cheaper than the roasting method. Details will be found in Collins' "Metallurgy of Silver."

I have found that these mattes are as readily converted to bullion by the following process: Grind the matte, and add in an iron pot enough concentrated sulphuric acid to react with all the silver and copper as follows:



On heating the mixture gently part of the matte is converted to sulphates, and a little sulphur comes off with much  $\text{SO}_2$ . The dry product is transferred to a melting crucible, and treated, when the mass melts down quietly, to copper-silver bullion.

**Melting with the addition of sulphur for matte and slag.**—In case the slime contains little bismuth, or only small quantities of silver, the direct fusion of the partially-oxidized slime suffers from two disadvantages. One is the high temperature necessary to melt the doré bullion, which is too high for antimony trioxide to remain as liquid, and on the other hand, either the silver is apt to go into the slag, or the doré contains too much lead and antimony.

A very neat melting method consists in adding sulphur to the air-oxidized slime, in about sufficient quantity to reduce any  $\text{Sb}_2\text{O}_5$  to  $\text{Sb}_2\text{O}_3$  and to form a silver-copper matte with the copper and silver of the slime.\*

As an example Trail slime containing, when dried,

Ag. ....	14.6%
Cu. ....	8.1%
Sb. ....	27.60%
Pb. ....	16.0%
As. ....	27.0%
Au. ....	34 ozs. per ton.

was melted with various amounts of sulphur from 8 to 12%. 8% was found to be about right. When the slime was given a slight further roast as a preliminary, a little more sulphur was used.

100 grams roasted slime and 10 grams sulphur, melted in a porcelain crucible, gave

TABLE 32.

Matte, 43 Gr.		Slag, 45 Gr.	
Ag. ....	34.0%	Cu. ....	0.2%
Cu. ....	19.2%	Pb. ....	12.1%
Pb. ....	24.8%	Sb. ....	51.4%
S. ....	13.9%	As. ....	5.2%
Au. ....	.25%	Fe. ....	3.0%
Sb. ....	5.8%		

Other mattes from the same slime contained:

TABLE 33.

Ag. ....	41.7%	38.1%	46.8%
Cu. ....	23.2%	21.8%	26.3%
Pb. ....	....	17.5%	5.8%

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\* Patent applied for.

100 grams of the unroasted but thoroughly oxidized slime gave with 7 grams of sulphur 35 grams of matte and 46 grams of slag. This matte contained less lead (about 5%) and less antimony.

The melting temperature was low, about 600° C. The matte should have no action on iron, and the slag might not either, so I tried a cast-iron pot for melting.

400 grams of slime and 28 grams of sulphur were added to the red-hot pot, and melted down. Large quantities of arsenic came off. The product consisted of 140 grams of matte with considerable metal intermixed, and about 190 grams of slag.

Another melt with 32 grams sulphur gave a product with no metal, but the cast was spoiled, and the products melted over again, with the addition of a few grams of sulphur. Products were about 160 grams matte and 165 grams slag.

After these three melts the pot shows no sign of wear. The last slag, however, analyzed 8.25% iron as against 3% when melted without access of iron. On the other hand, the fusion in an iron crucible gave a slag lower in silica, as of course would be expected.

Treatment of the slag: (1) This has been reduced to hard lead by smelting with litharge and carbon, from which first the lead may be extracted electrolytically, see page 55, and the antimony residue refined with the fluoride solution.

(2) It can be leached, after grinding, with hydrofluoric acid for antimony fluoride solution. The action of hydrofluoric acid is rapid and evolves considerable heat. The antimony can be deposited from the fluoride solution, to which sulphuric acid should be added. If the hydrofluoric acid



used contain also sulphuric acid, the residue will consist mostly of lead sulphate.

(3) The slag may also be leached after grinding with dilute nitric acid. After several hours' action the residue consists of yellow antimony trioxide and the solution contains lead nitrate. The production of lead nitrate as a by-product of a lead refinery is analagous to the production of copper sulphate by a copper refinery.

(4) The slag can be reduced to metal electrolytically, either with a fused electrolyte as lead chloride, see page 66, or with an aqueous electrolyte, as sulphuric acid solution. The following experiment illustrates the latter:

100 grams of slag containing about 50% antimony, 8% iron, 5% arsenic, and 15% lead, were ground rather fine, say 30 mesh, and placed in a shallow lead pan about 3 by 4 inches and about 1 inch deep. 25% sulphuric acid was added and a horizontal lead anode used about  $2\frac{1}{2}$  by  $3\frac{1}{2}$  inches, wrapped in cloth and about  $\frac{1}{2}$  inch from the slag. The current varied from three to six amperes, equivalent to a current density 40-80 amperes per square foot. During most of the run no gas was seen to rise from the cathode. About the middle of the run red antimony sulphide appeared in the electrolyte and floated around, the total quantity produced being 2.45 grams. Current necessary for complete reduction about 38 ampere hours, and when 36 ampere hours had passed  $H_2S$  came off for a while, and then was replaced by hydrogen. The appearance of  $H_2S$  would be a good indication of the end of the reaction.

Any iron of course went into solution as ferrous sulphate. It was thought that fluorine and silica might both be present in the slag and give rise to the formation of  $H_2SiF_6$  during

the action. Acids forming soluble lead salts cause a rapid corrosion of lead anodes in sulphuric acid, so I rather expected lead sulphate would drop off the anodes into the slag during the run, and used a cloth to keep any from dropping into the slag. The lead anode, however, was not attacked.

The cathode area was 10-12 square inches; anode area, 8.9 square inches; current 3-6 amperes. e.m.f. 2.25 to 2.9 volts.

TABLE 34.

Time, Hrs. Min.	Volts.	Amperes.	Amperes, Hours.	Remarks.
0.15	2.25	4.3	.....	No gas noticed coming from cathode.
0.30	2.25	3.5	.....	No gas noticed coming from cathode.
2.30	2.25	3.5	.....	No gas noticed coming from cathode.
2.45	2.45	3.0	9.85	No gas noticed coming from cathode.
5.35	2.50	3.5	31.67	No gas noticed coming from cathode.
9.28	2.60	3.0	31.25	Sb <sub>2</sub> S <sub>3</sub> suspended in electrolyte.
9.58	2.60	3.2	.....	Sb <sub>2</sub> S <sub>3</sub> suspended in electrolyte.
10.45	2.6	3.2	.....	Some H <sub>2</sub> S evolved.
11.35	2.75	4.6		
12.20	2.65	5.8		
12.45	2.65	5.0	44.93	
13.45	2.9	5		
15.05	2.7	3.6	.....	No H <sub>2</sub> S evolved.
16.25	2.8	3.5		
17.05	....	...	55	

The rise in voltage after about 12 hours and 45 minutes indicated the completion of the reaction.

The electrolyte contained some ferrous sulphate. Part of the former slag was cemented to the lead tray and part was loose. It had not changed much in appearance.

After washing, and before drying, part of the product was rapidly melted in a crucible, producing metal and no slag, showing good reduction. Another test was made and gave 15.5 gr. metal and 4.5 gr. slag. In the first test a clay cruci-

ble was used which probably had absorbed the small quantity of slag.

To reduce the 40–45 grams antimony and 15 grams lead in the slag would require about 40 ampere hours, which it will be noticed corresponds with the increase in voltage. The current efficiency appears from the slight evolution of hydrogen and from the above noted circumstances, to be quite high. The slag produced in melting may have resulted from oxidation during drying and fusion.

These slags may also be conveniently reduced to hard lead, by smelting with litharge or dross from the refined lead pot and carbon.

The extraction of the lead from the hard lead is achieved by refining with the fluosilicate electrolyte. Further experiments are necessary before it is possible to say whether it would be better to melt the antimony residue and refine electrolytically with the fluoride solution, or refine the antimony skeleton directly as anode in the same solution.

**Direct electrolysis with slime as anode.**—As the slime retains very often the form of the original anode, especially when the percentage of impurity is rather high, say 3 to 10%, the proposition of placing the anode with the slime still adhering in an appropriate solution, and making it the anode, while one of the principal metals contained goes over to the cathode, seems promising.

Some means of removing or washing out the lead electrolyte in the slime, worth on the average, say \$2.25 per ton of lead refined, is very necessary. In time, with frequent changes of wash-water in a tank containing a set of anodes, this solution could be removed to any desired extent by the simple action of diffusion. We tried another method, namely,



connecting up the anode with attached slime as cathode in a solution of fluosilic acid, with carbon anodes. Passing the current deposits some lead in and on the slime, and lead peroxide on the anode, while the valuable  $\text{SiF}_6$  present of course moves away from the slime, now cathode, into the solution. A removal is possible in this way, but our result from the following experiment could not be called successful.

The original lead alloy contained lead 90%; arsenic 5%; antimony 3.0%; copper 1%; silver 0.7%, and Bi 0.05%, and was refined with an electrolyte containing 8.05 grams lead and 15.9 grams  $\text{SiF}_6$  per 100 cc. The anode was originally about  $\frac{7}{8}$ " thick, and was treated until the lead was practically all removed.

The residue was then made cathode in a solution containing 6.15 grams  $\text{SiF}_6$  per 100 cc. and no lead. Volume of solution 715 cc.=46.5 gr.  $\text{SiF}_6$ . Anodes of carbon ( $\frac{3}{4}$ " round electric light carbons).

TABLE 35.

Time.	Amperes.	Volts.	Amperes per Square Foot.	Temperature.
9.30	1.82	2.45	12.5	16° C.
9.45	1.82	2.40	12.5	
10.20	1.45	2.25	9.9	17° C.
11.30	1.93	2.40	13.2	19° C.
4.00	1.45	2.40	9.9	20° C.

The  $\text{SiF}_6$  in the solution increased by only 8.5 grams instead of 10.7 grams or more present in the slime.

The volume of the pores in the slime treated was 67 cc. While sufficient current was passed to remove 29.1  $\text{SiF}_6$  grams at 100% efficiency, only part of that present was actually removed, with an efficiency of about 30%.

It is possible to so choose the electrolyte for refining the attached slime, that the fluosilicic acid and lead fluosilicate of the slime is not lost, but may be recovered from the second electrolyte.

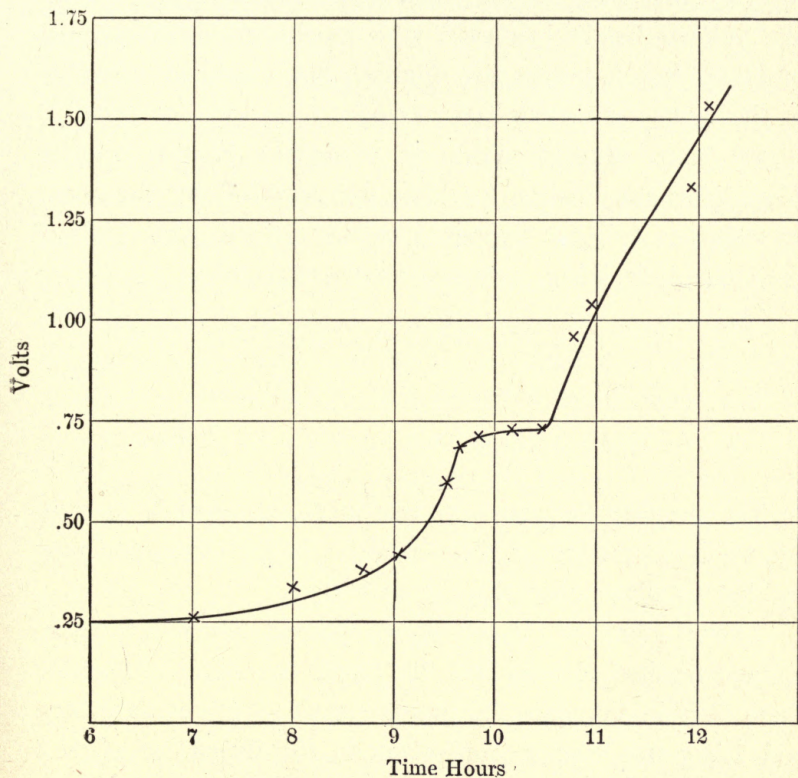
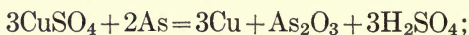
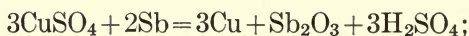


FIG. 10.

EXPERIMENT.—Bullion containing arsenic 5%, antimony 3%, and copper 1% in the shape of an anode,  $3\frac{1}{4} \times 1\frac{1}{4} \times \frac{1}{8}$  inches, was electrolyzed until 300 grams lead was dissolved out, or about 350 grams of alloy decomposed. The core was then about  $\frac{3}{8}$ " thick. The slime was scraped off one side for

another experiment and the other half made anode in a hot solution containing 15%  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$ . Temperature about  $70^\circ \text{C}$ . On the start with a current of 1 ampere the voltage was .26, rising after about six hours as plotted in Fig. 10. The copper deposited remained good, though the voltage finally increased very much. A small quantity of  $\text{Sb}_2\text{O}_3$  was found in the solution, but nearly all remained in the slime, with some lead sulphate.

Of course the concentration of copper in the solution continually got smaller, for little was supplied by the anode to make up for that deposited at the cathode, the result of the electrolysis being expressed by these reactions:



The peculiar flat place in the curve corresponds in voltage to the formation of silver sulphate in the slime, and may be due to silver dissolving at that time.

Twelve grams of copper were deposited, about 9.5 before voltage reached .4 volt and 2.5 grams thereafter. Roughly there were in the slime 7.5 grams arsenic, 6 grams antimony, and 1.5 grams copper, equivalent to the deposition of 16.0 grams of copper, so that the oxidizing efficiency at the anode was about 75%.

The anode, with the slime still remaining on it, was put in dilute  $\text{HF} + \text{H}_2\text{SO}_4$ , with the idea that the antimony would dissolve out and the slime drop off, which would be a good thing in practice as it would save cleaning the anode scrap. However, the slime did not fall off, perhaps because the  $\text{HF}$



used was too small in quantity, theoretically only just about sufficient being used to form  $\text{SbF}_3$ , while an excess should have been used on account of the long time necessary to complete the reaction.

To make use of this simple process the following conditions are necessary:

(1) Anodes containing enough impurity to cause the slime to hold together quite firmly. (2) Rather thin anodes, in order that the electrolytic action can penetrate all the slime. (3) A supply of copper sulphate, or copper containing material, as matte, which could be treated with the dilute sulphuric acid produced in the process to make copper sulphate solution. (4) Recovery of  $\text{H}_2\text{SiF}_6$  from the copper sulphate sulphuric acid solution, as by precipitation with  $\text{K}_2\text{SO}_4$ , and distillation of the sodium fluosilicate with sulphuric acid to recover  $\text{H}_2\text{SiF}_6$ .

The arsenic of course dissolves in the hot solution and can be crystallized out merely by cooling. Analysis of the figures noted in the experiment indicate that the electrolysis goes smoothly, as long as metallic arsenic remains in the slime, and thereafter the voltage rises.

The recovery of antimony and hydrofluoric acid would be by the usual method described in Chapter III.

Such a slime process can be carried out with other solutions than that of copper sulphate and sulphuric acid; for example, antimony or copper fluoride-hydrofluoric acid solution which possesses the advantage of taking nearly the entire slime; that is, the arsenic, antimony, and copper into solution, while depositing copper at the cathode.

In refining bullion containing Pb 65.37%, Bi 7.32%, Sb 19.51%, As 5.85%, and Ag 1.95%, an anode covered with

slime was electrolyzed in a solution of  $\text{SbF}_3 + \text{HF} + \text{Na}_2\text{SO}_4$ , containing about 4% antimony. The cathode deposit was black and spongy and the e.m.f. very high, so that it was not a success. This may be due to the fact that the solution contained  $\text{SO}_4''$ , which I afterward found out was a mistake. When  $\text{SO}_4''$  is present the antimony is converted at the anode partly into insoluble basic insulating compounds, while if the only anion present in  $\text{F}'$ , the antimony goes straight into solution as  $\text{SbF}_3$ .

An alloy containing Pb 65.56%, Ag 1.94%, Cu 1.94%, Bi 6.84%, As 5.47%, and Sb 18.24%, after removing the lead electrolytically, was treated in the same way, only all  $\text{PbSiF}_6$  was removed by steeping the anode, after extracting lead, in hot water. The antimony electrolyte contained 6.4 grams Sb, as  $\text{SbF}_3$ , 5.4 grams HF and 5 grams  $(\text{NH}_4)_2\text{SO}_4$  per 100 cc.

The results are given in Table 36.

TABLE 36.

Time.	Amperes.	Volts.	Amperes, Sq. Ft.	Back E.M.F. Volts.	Remarks.
0.5 hours	0.36	0.42	6.7	0.23	Fair deposit.
5.0 "	0.38	0.38	6.1	0.14	
8.0 "	0.34	0.38	5.4	0.14	
14. $\frac{1}{4}$ "	0.29	0.34	4.6	0.15	
17. $\frac{1}{4}$ "	0.33	0.38	5.3	0.18	
17. $\frac{1}{4}$ "	0.33	0.36	5.3	0.18	Fair deposit. Powdery deposit.
26. $\frac{3}{4}$ "	0.28	0.38	4.5	0.18	
136 "	0.10	1.24	1.6	....	

The slime was irregularly attacked, being very hard in places and very soft in others. The core had been attacked seriously under the soft spots, showing the current was applied for too long a time.

**Fusion to alloys and electrolytic refining.**—In the paragraph on “fusion”, page 64, a description is given of an easy method of eliminating lead from the alloy if desired. It is then possible to eliminate lead in the first place, so if the presence of lead is objectionable on account of any electrolytic process desired to be used, it may be disposed of on the start.

The treatment of the alloy by electrolysis will of course depend on the composition of the alloy. If it should be mostly bismuth, as it might be in working up bismuth alloys, it could be electrolytically refined with a solution containing about 10% free methylsulphuric acid and 4% of bismuth as methylsulphate. This makes an excellent electrolyte for refining bismuth.\* If the alloy is mainly silver, copper, or antimony, refining with the solution appropriate for that metal could be adopted.

For the usual case, producing a mixed alloy with relatively large amounts of silver and antimony and important amounts of lead, copper and perhaps bismuth, this method does not seem to offer sufficient advantages over the usual wet methods of treatment. In this case it would be advisable to add outside antimony, silver, or copper that would be refined anyway, to make a preponderating proportion of one metal, which is always desirable in electrolytic refining. Of the three metals copper offers the chief advantages. Copper for refining is usually available, it produces the most satisfactory cathode deposit, and comes down as pure metal, and most important of all the resulting slime was found to

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\* According to Mohn, bismuth trichloride, with 10% free HCl, is used successfully for this purpose. *Electrochemical and Metallurgical Industry*, August, 1907.



contain only traces of copper or antimony, and thus a sharp separation and complete recovery of the metals is easy. There is no difficulty in depositing pure copper in presence of antimony fluoride, even though the percentage of copper falls to a very low figure, if a brisk circulation is kept up. This then affords a separation, copper on the cathodes, antimony collects on the solution and continually increases in amount while copper diminishes, and silver, bismuth, and gold constitute the slime.

In one experiment the alloy, which contained approximately 30% silver, 45% antimony, 14% bismuth, and 9% copper, was melted in a crucible and two and one-half times its weight of copper added, under a cover of salt, and then contained 8.6% silver, 12.9% antimony, 4% bismuth, 74% copper. There was no volatilization during the process, and the alloy was very much more readily fusible than copper. The maximum temperature during the melt did not exceed 800° C. probably.

The alloy was electrolytically refined with a solution containing  $\text{CuF}_2$ ,  $\text{NaF}$ , and  $\text{HF}$ , and no  $\text{H}_2\text{SO}_4$ . Copper was deposited in a satisfactory condition on the cathodes, though it was not as solid as the copper from a sulphate solution. The cathodes were bright and clean looking, but the crystallization was coarser than is obtained with a sulphate solution.

Some white bismuth compound separated on the bottom of the tank during electrolysis, and the anode slime contained the remainder of the bismuth, as well as the silver, and 1% copper and 2.5% of antimony. The extraction of antimony and copper was then approximately 96% and 99.7% of that present respectively. The slime would be melted for doré

bullion and a bismuth slag, and the solution, which continually diminishes in copper content while antimony increases, would have to be treated for metallic antimony and regeneration of the copper fluoride; for example, by precipitating the remaining copper by running the solution through broken antimony, depositing antimony from the solution with a lead anode and neutralizing HF in the solution with copper oxide, roasted matte, etc.

**Wet treatment with regeneration of the solutions.**—By getting the metals of the slime into the solution in some way and electrolyzing the solution for the contained metals, and simultaneously producing an anode product which may be used in oxidizing further quantities of slime, important advantages may be secured. It not being necessary to dry the slime, the danger of loss from dusting and the physical discomfort of working with such poisonous, penetrating dust, are avoided, as well as the involved expense. For any wet treatment process the raw slime is better suited than it is after drying on account of its more open nature. The chemicals required, an important item in most methods, are reduced in amount, only enough being required to make up for mechanical losses. A certain amount of electric energy is needed, but this is not great. It will be noticed that in most of the other methods outlined, steps are introduced which require electric energy, so this item applies to practically all methods anyway, and is not therefore a disadvantage peculiar to this class of processes.

The acids, the salts of which have been used in the solutions, are few in number, the choice being necessarily limited. The ideal acid to use is the same as that used in the lead depositing electrolyte, that is, fluosilicic acid. A combina-

tion of lead peroxide as oxidizing agent and fluosilicic acid solution has an important advantage on the score of simplicity of the whole. With their use it would not be necessary even to wash the slime, as the two electrolytes, slime treating and lead depositing, are the same, and after suitable purification of the slime electrolyte can be exchanged when convenient.

With the fluosilicate electrolyte we may use lead peroxide as oxygen-carrier, and the other metal that has been used as oxygen carriers from the anode to the slime is iron, passing from the ferrous to the ferric state, and back again.

The production of ferric *fluosilicate* has not been seriously attempted, and there are certain objections to its use. One comes from the fact that in electrolyzing the solution with insoluble anodes of carbon for ferric fluosilicate, silica deposits on the anodes and stops the oxidation of the iron, while if hydrofluoric acid, in small quantity, is used to prevent this, the difficulties in the way of a successful diaphragm, materials containing silica being barred, have prevented any serious attempt in this line.

Fluosilicic acid being unsuitable, we find that sulphuric, hydrochloric, and hydrofluoric acids are cheap enough to be considered from slime-treating solutions. The question of tanks is an important one, on which depends to a large extent the choice of available acids. Until recently, there appeared to be no suitable tank for working with strongly acid chloride solutions (to keep  $\text{SbCl}_3$  from decomposing). However, a concrete tank, saturated with sulphur, described in Chapter VII, is not acted on by hydrochloric acid.

Ferric *chloride* has been used in experiments on antimony slime from refining hard lead. The electrolyzed solu-



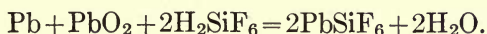
tion contained beside hydrochloric ferrous chloride and antimony trichloride, which yielded antimony on the cathode and ferric chloride at the anode.\*

Ferric *sulphate* is an ideal solution in some ways, on account of the cheapness with which it may be produced and the ease of handling it in lead-lined tanks. It also has an advantage in separating copper and arsenic in solution, from antimony hydroxide and silver in the undissolved portion.

Hydrofluoric acid may also serve as a basis of the solution, and ferric *fluoride* be formed at the anode as oxidizer. Hydrofluoric acid may also be used in connection with ferric sulphate, when the antimony will go into solution as antimony trifluoride.

The use of the *insoluble* anode product, lead peroxide, has also been tried. Lead peroxide is easily obtained in quantity in dense scales and plates by electrolyzing lead fluosilicate solution with a graphite anode.

Lead peroxide and metallic lead, copper, etc., in slime react with lead peroxide in the presence of fluosilicic acid, for instance, to form fluosilicates.



**Ferric sulphate process.**—This is a neat process, and has been the subject of a great deal of experimenting. It is applicable to slime from copper refining as well as to lead slime. In the treatment of copper refinery slime it is apt to find a large use. The description may also prove of interest in connection with the Siemens & Halske process for copper ores and matte.†

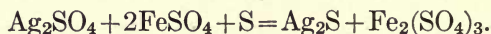
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\* A. G. Betts, Trans. Am. Electrochemical Society, Vol. VIII, page 188.

† Borcher's "Electric Smelting and Refining." 2d. Eng. Ed., page 260.

Ferric sulphate is a very soluble salt, of which a syrupy solution containing 10% Fe'' may be readily prepared. This is too strong for work with slime, principally on account of the less solubility of the resulting ferrous sulphate. Solutions used for slime treating should contain about five volume per cent of iron.

Ferric sulphate solution reacts with slime very readily, oxidizing metallic copper and cuprous sulphide to copper sulphate, antimony to hydrated trioxide, arsenic to arsenious acid, bismuth to basic sulphate, finely-divided lead to lead sulphate, and when hot converts silver to silver sulphate. The complete oxidation of silver is difficult or impossible on account of the reducing action of the ferrous sulphate formed. Practically, to dissolve one-half to two-thirds of the silver in slime requires the use of a considerable excess of ferric sulphate, so that the process is simplified in some respects by only using enough ferric sulphate to oxidize the other metals. When slime contains sulphur or sulphides, which it almost always does, especially copper slime, the solution of silver is hindered or entirely prevented. Apparently in the reaction between ferric sulphate and silver little or no energy is liberated and the presence of finely-divided sulphur, combining with the silver, can even reverse the action giving



Tellurium is dissolved by ferric sulphate and may be precipitated out on metallic copper, as a greasy, black coating. Selenium and gold are not dissolved from slime by ferric sulphate.

As the solution is prepared by electrolysis, and it is advisable to have a solution of as high conductivity as possible, the ferric sulphate used will contain some free sulphuric acid, 2-5%, and some ferrous sulphate, usually equivalent to 1% ferrous iron,  $\text{Fe}''$ .

From the reactions taking place, it will be seen that the process is not entirely cyclic. The reaction of the copper of the slime,  $\text{Cu} + \text{Fe}_2(\text{SO}_4)_3 = \text{CuSO}_4 + 2\text{FeSO}_4$ , is directly reversed in the electrolytic tank, so, as far as copper is concerned, the same solution could be used over and over again without any additions being made to it. In treating copper slime, consisting largely of  $\text{Cu}_2\text{S}$  and silver, this condition is quite well realized.

The reaction on antimony and arsenic, which consumes a good percentage of the ferric iron used, is not reversible. Oxygen is removed from the solution in the insoluble antimony hydrate, and arsenic removes oxygen from the cycle though not from the solution. Lead removes  $\text{SO}_4''$ , but not in large or serious quantity.

For many slimes, containing say 30% Sb, 15% Cu, 10% As, beside lead and silver, the amount of iron reduced by antimony and arsenic would approximate two-thirds of the total.

Several methods exist of adding combined oxygen to the solution to make up the deficiency, but the best seems to be the addition of copper oxide in some form, especially as roasted copper or copper-lead matte. As the copper is recovered as electrolytic metal, from a raw material, the process may be credited with part of the enhanced value of the copper. With the addition of copper oxide from any source, and crystallization from the solution of arsenious acid, the solution may be used over, if mechanical losses are made up.



Another method of supplying oxygen consists in air-drying the slime before treatment with ferric sulphate, which introduces considerable oxygen, but this suffers from several objections, such as the formation of hard lumps which are attached with difficulty and greater expense and losses.

The separation of the metals by the sulphate solution is not perfect, principally because antimony and bismuth hydroxides or basic salts are not entirely insoluble in the solution. The solubility of  $\text{Sb}_2\text{O}_3$  in the solution is approximately 1.6 grams per litre cold and 2.2 grams hot. Variations in the percentage of sulphuric acid have little influence on the solubility of antimony. The amount of bismuth dissolved is about 1.5 grams per litre, and none separates on cooling. From other results obtained, the solubility of bismuth is somewhat greater in the cold solution, on account of change to another series of so far uninvestigated salts in which bismuth has greater basicity.

For the sake of example, let us assume that one ton of lead contains 7.4 lbs. silver, 2 lbs. bismuth, 4 lbs. arsenic, 10 lbs. copper, 20 lbs. antimony, while 5 lbs. of lead will also remain in the slime.

Ferric iron required is readily calculated by the use of factors, as given in Table 37.

TABLE 37.

For silver	None.
" bismuth $2 \times .81 =$	1.62 lbs.
" arsenic $1 \times 2.24 =$	8.96 "
" copper $10 \times 1.76 =$	17.60 "
" antimony $20 \times 1.40 =$	28.00 "
" lead $5 \times .54 =$	2.7 "
Total . . . . .	58.88

This amount of ferric iron is contained in about 23 cubic feet of electrolyzed solution. Allowance must be made for the fact that the action is not entirely complete. Usually not all the copper and arsenic present dissolve, but only about 90%. Taking account of the solubility of bismuth and antimony, and of copper already in solution to the amount of 10 grams per litre, and used to boil out traces of silver and reduce excess of  $\text{Fe}^{++}$ , the distribution of the products is about as follows:

TABLE 38.

In Solution.	In Sediment After Cooling.	In Residue.
All Iron.	Lbs.	All Lead.
2.35 lbs. antimony	.85 antimony	16.8 lbs. antimony
1.8 " bismuth	.....	.2 " bismuth
26.0 " copper	.....	1 " copper.
8.1 " arsenic	.....	.9 " arsenic.

The solution also contains fluosilicic acid present in the slime on account of not entirely complete washing. This is a troublesome compound to have present, as will be explained elsewhere, on page 109.

The sediment can be put in a charge of fresh slime. The residue has then to be washed rather free of iron and copper sulphate, and is then treated with a solution of hydrofluoric and sulphuric acids, which may vary largely in composition, about 5% sulphuric acid and 5-10% hydrofluoric acid being satisfactory. The result is the solution of approximately 95% of the antimony and arsenic still remaining, with a little copper and iron. Silica also dissolves. The following analyses are of air-dried Trail slime treated experimentally. In the first column is given the analysis of the air-dried slime,

in the second column the same after treatment with ferric sulphate, and in the third column the same after treatment with HF solution:

TABLE 39.

H <sub>2</sub> O.....	14.5%		
Au.....	34.5 ozs.	36.44 ozs.	69.32 ozs.
Ag.....	15.9%	16.2%	31.9%
Cu.....	9.5%	.8%	1.28%
Pb.....	16.0%	17.6%	33.1%
Sb.....	25.91%	25.03%	3.72%
As.....	5.96%	1.2%	Nil.
SiO <sub>2</sub> .....	2.2%	1.8%	0.8%

The distribution of the products in this case were calculated from the analyses to be about as follows:

TABLE 40.

In Copper-iron Solution.	In Fluoride Solution.	In Residue.
No silver *	No silver *	100% silver
No gold *	No gold *	100% gold
No lead *	No lead *	100% lead
92% of the copper	1% of the copper	7% of the copper
8.5% of the antimony	84.5% of the antimony	6.75% of the antimony
81% of the arsenic	19% of the arsenic	No arsenic
23% of the silica	59% of the silica	18% of the silica

\* Known from tests of solutions.

With the slime which has not been dried the results are somewhat better than the above, as the inevitable result of drying is the formation of hard lumps which it is hard for the solutions to penetrate.

Usually silver dissolves, as a small excess of ferric sulphate is always used, and before filtration the solution and suspended slime are agitated in presence of metallic copper until the excess of ferric sulphate has been reduced and all the silver removed from the solution. At a boiling temper-



ature this takes from 2 to 10 hours according to the copper surface exposed, and the amount of ferric sulphate in excess. An exposure of about 4 square feet of copper for each cubic foot of solution is sufficient for moderately quick work.

Settling and filtration is found to be much easier and quicker after silver has been removed. The solution settles clear in a short time and most of it can be drawn off without filtration. The residue may be washed by decantation to best advantage with hot water, or filtered in a press or on a horizontal cloth resting in a shallow tank with a perforated or grooved wood or lead bottom. Centrifugal machines are also used for this kind of work. If the material cools very much during filtration it clogs up from separation of antimony oxide.

The extraction of silver requires a considerable excess of ferric sulphate, and even then with most slime the extraction of silver is very incomplete. If the silver could be dissolved and precipitated on copper in a separate tank, the expense of melting silver twice and parting would be saved. A temperature of 95–100° gives a much better extraction of silver than one of 80°. This was shown in an experiment on slime containing 79% Ag; 12.6% Cu; 4.12% Sb; 88% Bi; 3% Pb, from refining rich lead with 10% and 15% silver. The precipitated silver was washed in this case with HCl to take out traces of  $\text{Sb}_2\text{O}_3 + \text{Bi}_2\text{O}_3$ . A large excess of ferric iron was used, but it is doubtful if this made any great difference in the result. The use of a considerable bulk of solution had more influence probably. Particulars are given in Table 41.

TABLE 41.

No.	Weight of Slime.	Volume Solution.	Fe'' Used.	Time.	Temperature.	Residue.
1	45 gr.	2500 cc.	50 gr.	3¼ H.	80-85°	13.5 gr.
2	45 gr.	2500 cc.	50 gr.	3¼ H.	95-99°	6.4 gr.

No.	Precipitated Silver.	Contains Before Melting.	Silver Extraction.
1	25.7 gr.	98.71% Ag	71.4%
2	33.2 gr.	99.65% Ag	93.0%

The treatment of copper slime with ferric sulphate is very successful in removing copper quickly. With slime from blister copper anodes, there is too much sulphur present to allow of the solution of much if any silver. Several experiments have been made on slime analyzing Cu 53.29%; Ag 12.90%; Bi 1.55%; Sb 3.30%; As 1.15%; S 11.96%; Te 1.97%; Se .26%; Pb trace; gold and moisture not determined. See Table 42.

TABLE 42.

No.	Slime Taken.	Fe'''.	Temperature.	Volume.	H <sub>2</sub> SO <sub>4</sub> .	Residue.
1	200 gr.	161 gr.	90°	.....	.....	122 gr.
2	100 gr.	100 gr.	85-92°	1 200 cc.	5%	325 gr.
3	700 gr.	750 gr.	85-90°	9 500 cc.	4.2%	} See Table 43.
4	700 gr.	750 gr.	85-92°	10 000 cc.	4%	

The residue was treated with caustic-soda solution to extract the sulphur, antimony, selenium, and tellurium if possible. Traces of tellurium dissolved out, but no selenium.

TABLE 43.

No.	NaOH.	Volume.	Temperature.	Residue.	Fusion.	Product.	Ag in Button.
2	30 gr.	150 cc.	Boiling	19.7 gr.	10 gr. nitre 7.5 gr. soda	Dore matte and slag	12.22 gr.
3	200 gr.	2000 cc.	"	159.5 gr.	90 gr. nitre 100 gr. soda	Dore matte and slag	} 163 gr.
4	200 gr.	2000 cc.	"	177 gr.	90 gr. nitre 100 gr. soda	Dore matte and slag	

Analysis of doré from 3 and 4, Ag 86.55%; Bi 5.37%; Cu 5.99%; Au 1.62%; Te .16%; Se trace; Pb nil; Sb trace; Cu nil; As nil.

The residue from No. 1 was melted direct to matte, without treatment with NaOH. Matte weighed 48 grams. Contained 12.7% S; 53.6% Ag calculated. Probably a great deal more caustic soda was used than was entirely necessary. Probably 80 grams of caustic for 700 parts slime taken would have done just as well. Milk of lime would act similarly to caustic soda and be cheaper.

In treating copper slime with ferric sulphate, the process works quickly and completely at a temperature of about 90°; at 100° the liberated sulphur sticks together and hinders the reaction. Only a slight excess of ferric iron should be used, and the excess reduced by suspending copper plates in the solution before removing it from the insoluble residue.

Returning to the consideration of lead slime-treatment, the solution, after removal from the slime, now containing ferrous sulphate, cupric sulphate, arsenious acid, and sulphuric acid, beside smaller quantities of arsenic, bismuth, silica, and fluosilicic acid, is to be electrolyzed for metallic copper and regeneration of ferric sulphate. A separate treatment of the solution with copper oxide, metallic copper and



air, or copper matte, is necessary, unless the slime being treated should have been air-dried, and say two-thirds oxidized.

The electrolysis of the solution takes place at about  $40^{\circ}$ , and on cooling to this temperature or a little lower about 10 grams antimony oxide per litre and excess of arsenious acid above that required to saturate the solution at this temperature (say 2%  $\text{As}_2\text{O}_3$ ) crystallize out. This cooling takes care of the arsenic of the slime, the solution, after reaching a concentration of about 2%  $\text{As}_2\text{O}_3$ , thereafter depositing that removed from the slime. The arsenic crystallizes as bright, hard crystals. The solubility of  $\text{As}_2\text{O}_3$  in the hot solution is about one part in ten parts solution, and at  $20^{\circ}$  one part in 100 parts solution, having therefore a large variation for difference in temperature. There are two varieties of  $\text{As}_2\text{O}_3$ , but we have here to do, at least in the cold, with the crystalline variety, of which the solubility is ten parts in 100 parts hot water and 1.7 parts in 100 parts cold water (Comey's Dictionary). The solubility in reduced iron solution is not very different.

The electrolysis of solution containing iron and copper for the production of a copper deposit and a solution of ferric sulphate was first proposed by Body.\*

Siemens and Halske† proposed a process in which the ferric sulphate was used to attack metallic copper and copper sulphide and the solution then brought back to the electrolytic cell for the recovery of the copper and the ferric sulphate. Difficulties were met by Siemens and Halske in the electrolysis,

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\* U. S. A. Patent 338150. Jan. 5, 1886.

† German Patent 42243. Sept. 14, 1886. English Patent 14033. Nov. 1, 1886.

particularly the carbon anodes were corroded and the yield of ferric sulphate was low. The corrosion of the carbon anodes was a fatal difficulty. I found that the anodes could be made to last permanently if they were kept in constant motion through the solution.\*

The electrolysis of the reduced iron solution has been made the subject of a special study to determine the effect on the current density and voltage of variations in temperature and chemical composition.

The electrodes used in the test were each of graphite, and the anode was kept in back-and-forth motion through the electrolyte by means of a crank. If the anode stopped it

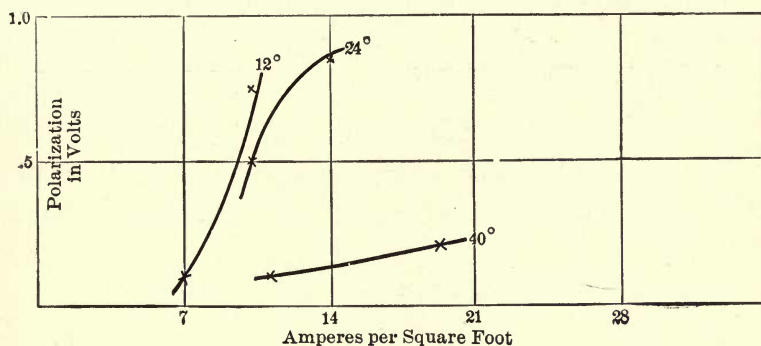


FIG 11.—SOLUTION O.

polarized in a short time, and oxygen was evolved on the anode and little or no ferric iron formed. As the anode reaction was the only one with which difficulty was experienced before the requirements of the case were understood, the deposition of copper at the cathode was disregarded, and a solution electrolyzed containing ferrous sulphate, copper sul-

\* U. S. A. Patent 803543. Nov. 7, 1905.

phate, and sulphuric acid, and in some cases also ferric sulphate, without a diaphragm.

The results indicate that the effect of temperature is the most important. The results are plotted as Figs. 11 to 17. The ordinates represent the polarization in excess of the electromotive force required to carry out the oxidation of the iron.

Solutions were tested as follows:

TABLE 44.

Solution.	O	A	B	C	D
H <sub>2</sub> SO <sub>4</sub> grams per 100 cc. ....	1	2	3	5	9
FeSO <sub>4</sub> 7H <sub>2</sub> O " " 100 " .....	5	5	5	5	5
CuSO <sub>4</sub> 5H <sub>2</sub> O " " 100 " .....	12	12	12	12	12

The amperes per square foot refers to plane occupied by 1 inch carbon rods spaced  $1\frac{1}{8}$  inch centre to centre. For amperes per square foot of carbon surface, multiply by 1.09.

Tests were also made with the following solution:

TABLE 45.

Solution.	O'	A'	B'	C'	D'
H <sub>2</sub> SO <sub>4</sub> grams per 100 cc. ....	1	2	3	5	9
FeSO <sub>4</sub> 7H <sub>2</sub> O " " 100 " .....	5	5	5	5	5
CuSO <sub>4</sub> 5H <sub>2</sub> O " " 100 " .....	4	4	4	4	4
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> " " 100 " .....	10.7	10.7	10.7	10.7	10.7

The results are somewhat different, probably on account of the failure of copper to deposit on the cathodes in the second series where the reduction of ferric iron takes place



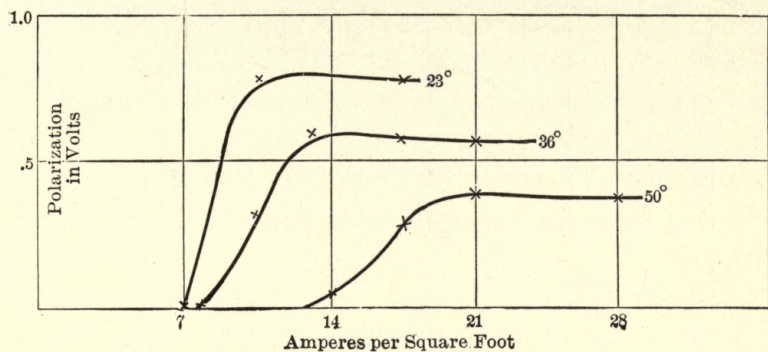


FIG. 12.—SOLUTION A.

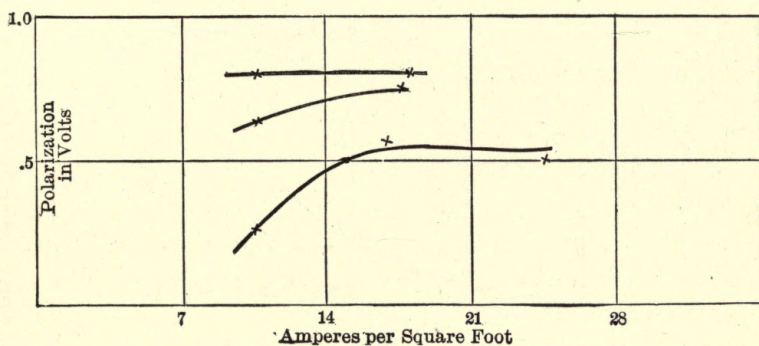


FIG. 13.—SOLUTION B.

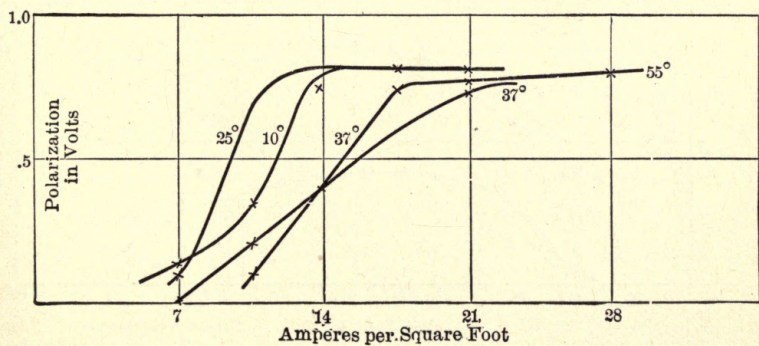


FIG. 14.—SOLUTION C.

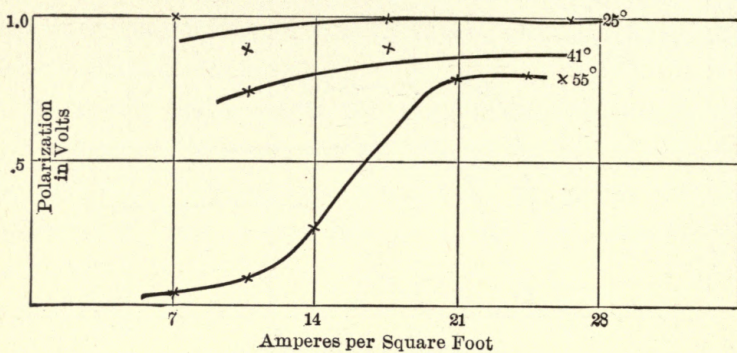


FIG. 15.—SOLUTION D.

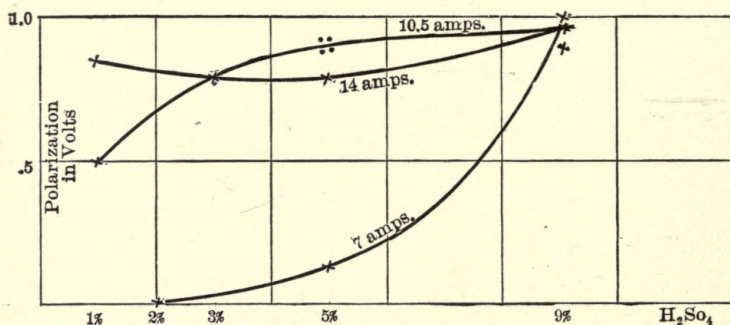


FIG. 16.—EFFECT OF SULPHURIC ACID AT 25° C.

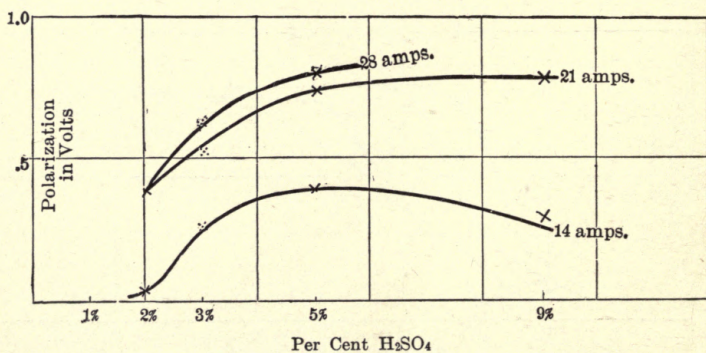


FIG. 17.—EFFECT OF SULPHURIC ACID AT 50°-55° C.



instead. I regard these latter results as showing the anode polarization best. See Figs. 18, 19, 20, 21.

The necessity of moving the anodes exists under the conditions studied in these experiments if polarization is to be prevented. However, I found that at a still higher temperature, near boiling, it is no longer necessary to move the anodes.\*

Of course, at lower temperatures, the anode rods might be left stationary if the relative motion between anode surface and electrolyte was maintained by rapid circulation,

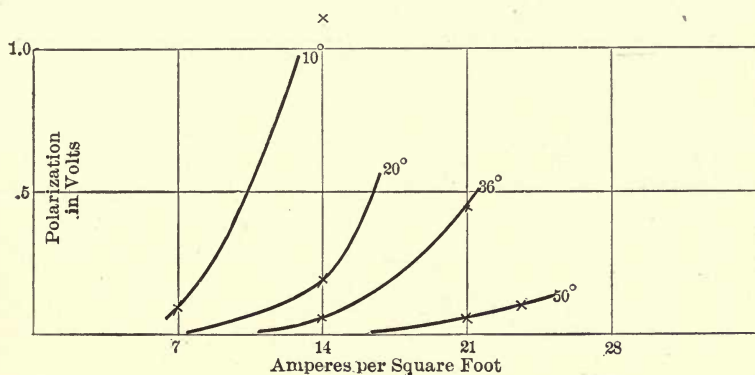


FIG. 18.—SOLUTION A'.

but it would have to be so rapid as to be impracticable on a large scale, in a tank of any ordinary construction.

It was found in some experiments on slime treatment that the anodes polarized in spite of everything that could be done, including increasing temperature and the velocity of the anodes. The anodes on taking out were slimy to the touch; after brushing off they would run some hours successfully and would then polarize again.

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\* U. S. Patent applied for.



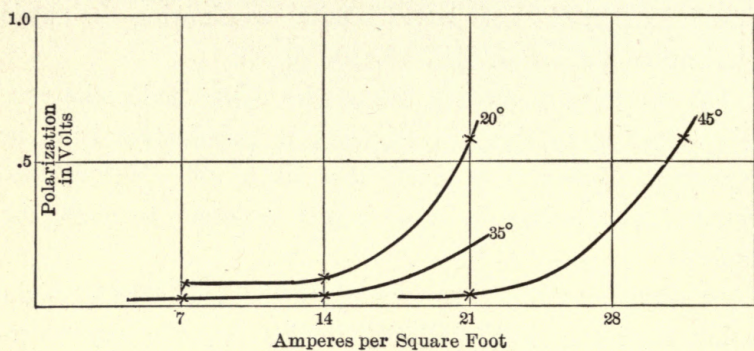


FIG. 19.—SOLUTION B'.

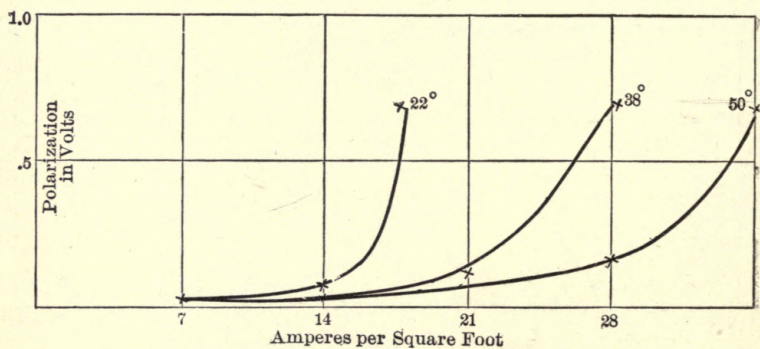


FIG. 20.—SOLUTION C'.

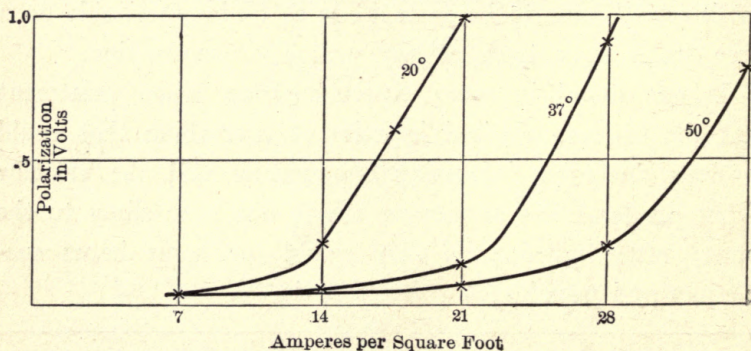


FIG. 21.—SOLUTION D'.

As the process has been worked continuously on other ferrous sulphate solutions than those from treating lead slime, an investigation was made to ascertain the cause of the trouble.

Pure solution of iron and copper sulphates and sulphuric acid were treated with various materials and electrolyzed. The presence of gelatine, tin, arsenic, antimony, bismuth, and soluble silica had no prejudicial effect.

Fluosilicic acid, on the other hand, caused polarization readily, and if the quantity added was at all large, a thick silica deposit would form on the anode. The coating from anodes used in working up solution from slime treating was tested and found to consist largely of silica.

For large scale work, the remaining serious question is one of diaphragms. For this process diaphragms of wood, about  $\frac{5}{8}$ " thick with  $\frac{3}{4}$ " to  $\frac{7}{8}$ " holes bored through as closely as possible, with holes filled with wet asbestos; asbestos boards  $\frac{1}{4}$ " thick, hardened by absorption of the right amount of sulphur; and pairs of perforated lead sheets with several thicknesses of asbestos between have been tried, and all have given success.

The disadvantage of the wood diaphragms has been that the plugs, if not put in tightly enough, drop out, or if the copper deposit gets spongy, which has happened when unreduced solution was fed in, the copper may grow into the plugs and on drawing the cathodes, a plug or plugs come too.

The disadvantage of the asbestos board hardened with sulphur is that it expands slightly when wet and warps. This difficulty, I believe, can be cured by soaking the boards a week or two before putting them in a tank. The resistance is quite a little higher, requiring perhaps .4 to .5 volt more to operate a tank than one with lead and asbestos diaphragms.

The disadvantage of the lead and asbestos boards diaphragm is the cost of the lead, and the necessity of operating the tank at a uniform temperature to prevent wrinkling of the lead.

These advantages would have to be weighed against each other before making a choice, but good success will result in the use of any.

To prepare hardened asbestos diaphragms of the above construction, asbestos "mill boards," which come in about 40-inch squares, should be placed flat on a floor, powdered sulphur sprinkled on evenly, and placed in an oven hot enough to melt sulphur, for an hour or more. The sulphur melts and is absorbed by the asbestos. The same operation is repeated on the other side of the boards. The hot board is cooled on a flat floor, giving a sheet of considerable stiffness and strength, that does not soften in water or acid solution, even after a long time. Care must be used not to fully saturate the board with asbestos, which would make it an insulator. The effect of the sulphur is to cement the asbestos fibres together. Two to three pounds of sulphur is found to be about right for 10 square feet of  $\frac{1}{4}$ " board.

For details of construction of lead-lined copper-iron sulphate electrolytic tanks, see Chapter VII. The catholyte only comes in contact with the lead lining in these constructions. The solution of ferrous and cupric sulphates and sulphuric acid, containing approximately 30 grams copper, 40-50 grams ferrous iron and 20-60 grams  $\text{H}_2\text{SO}_4$  per litre, is fed in a continuous stream into the cathode compartment, which stands in composition at about 10 grams copper, 40-50 grams ferrous iron and 20-60 grams  $\text{H}_2\text{SO}_4$ . An overflow about two inches below the top of the tank is provided for the anolyte,



averaging 8-10 grams ferrous iron, 30-40 grams ferric iron, 20-60 grams  $\text{H}_2\text{SO}_4$  per litre. The effect of feeding solution to the catholyte is to maintain the catholyte at a slightly higher level than the anolyte, so that the solution percolates through the diaphragm continuously, preventing back-flow of anolyte to the catholyte compartments. The anolyte is also found to be slightly heavier than the catholyte, for instance, 1.19 and 1.16 specific gravity respectively.

The tanks are built on the principle of placing a series of anolyte boxes, with catholyte spaces between each, and on the sides and bottom too. Circulation of the catholyte through the tank can be easily arranged and circulation of the anolyte is provided by siphons connecting each anolyte compartment to a trough on each side of the tank. This trough need not necessarily be placed outside of the tank, but can be fitted inside. Circulation is maintained by compressed air. The trough on one side serves as a feed to all the anolyte compartments, and the discharge takes place to the trough on the other side. The siphons are provided with an arrangement by which the air can be sucked out.

Serious attempts were made to electrolyze the solution in cells without a diaphragm, depending on the formation of a heavier ferric sulphate solution at the anode, which should settle to the bottom of the cell. This principle can be applied successfully in electrolyzing chloride solutions, but it will be difficult or impossible, I think, to use it in iron sulphate electrolysis.

The slime after treatment with ferric sulphate should be washed fairly well, as any iron and copper salts not washed out will accumulate in the fluoride solution used for antimony extraction. Copper can, however, be removed by

antimony as described in Chapter III, and the only effect of iron is to slightly diminish the current efficiency of the antimony deposition, but not very seriously.

The fluoride solution dissolves most of the antimony present, as well as the arsenic still remaining, and traces of bismuth and silica.

The solubility of bismuth in the fluoride solution, provided excess of acid is used, is very slight. Considerable quantities dissolve, if no excess of HF is used, and HF added to the solution in that case causes a precipitation of bismuth, probably as  $\text{BiF}_3$ . The amount of bismuth dissolved with excess of HF present has been variously determined from .008 to .010 grams per 100 cc.

The bismuth dissolved deposits out with the antimony, and on one occasion, treating high bismuth slime, the percentage of bismuth in the antimony was 0.67. This is the highest percentage yet observed, and is equivalent to .035 grams Bi dissolved per 100 cc.

The extraction of antimony with HF from the slime after treatment with ferric sulphate averages 95%, a temperature of 30–40° C. and excess of HF being desirable. The effect of  $\text{H}_2\text{SO}_4$ , which is also present in the solutions, seems to be insignificant. See Table 46.

TABLE 46.

Weight of Slime.	HF Excess.	Weight of Residue.	Temperature.	Slime.	Residue.	Extracted, Sb.
200 gr.	17%	107	20° C.	30.8% Sb	5.59% Sb	90.3%
100 gr.	200%	50.2	20° C.	30.8% Sb	3.99% Sb	93.5%
50 gr.	200%	26.	35–40° C.	30.8% Sb	2.38% Sb	96.1%
50 gr.	200%	26.2	30–40° C.	30.8% Sb	3.63% Sb	93.8%

No silver dissolves in the fluoride solution, probably on account of the presence of other unoxidized metals capable of precipitating silver. The antimony fluoride solution is treated with  $K_2SO_4$  or  $Na_2SO_4$  for removal of  $SiF_6$  and electrolyzed for metallic antimony and regeneration of HF. Particulars will be found on page 144.

The treatment of the insoluble residue has only been carried out by fusion to doré bullion. This fusion can be accomplished with various fluxes, but soda has been chiefly used as a flux in the experiments, which was a mistake. Fusion with silica is better, and gives a clean doré bullion. The sulphur and carbon in the slime are oxidized by the oxygen liberated when lead sulphate is decomposed by silica. The lead silicate slag can be smelted for the lead and traces of silver it contains.

The fusion may be conducted in reverberatories, or crucibles, though the latter is best, for no furnace refining is required.

A sample of doré bullion produced from Trail slime, containing in the first place approximately 30% Sb; 29% Ag; 6% As; 10% Pb; and 7% Cu, which had been treated with ferric sulphate and hydrofluoric acid, and then melted with soda, contained Ag 78.94%; Pb 17.56%; Au 2.08%; Cu .81%; Sb .47%; no As. Other melts with silica have produced far cleaner doré, containing, beside gold and silver, only traces of copper and lead.

The metallurgical recovery of the ferric sulphate process is excellent. 95 lbs. of Trail slime contained by corrected fire assay 445.83 ozs. silver and 3.7 ozs. gold. This was treated experimentally in some 8 or 10 batches, using the solutions over and over again, and notwithstanding some



accidents, the silver recovery was 443.85 ozs. and gold 3.65 ozs. The limit of accuracy of the gold assays was .1 oz., so probably the actual recovery of gold was as great in proportion, or greater than that of silver. The silver loss was less than  $\frac{1}{2}\%$ , and on the basis of uncorrected assay there would have been a gain of from  $\frac{3}{4}\%$  to 1%.

Copper scale for adding copper and oxygen to the iron sulphate solution is not to be recommended, as it contains too much metallic copper and cuprous oxide. Copper sulphate is rather too expensive, though it may only represent roasted copper matte plus sulphuric acid. The use of granulated copper in a tower, through which the acid slowly passes in the presence of air is permissible but slow, requiring a large stock of metallic copper. The copper is relatively more expensive than the same material in the form of roasted matte.

Methods of treating roasted copper matte for extraction of copper are well-known, the best description being that given by Hofmann.\* The material treated at Argentine, Kansas, contained 40% Cu and 12-14% Pb. It was ground to 50 mesh in a ball-mill, and roasted in Pearce turret furnaces. The roasted material was again ground to 50-mesh in a ball-mill and treated in tanks with stirring-gear, with water and sulphuric acid. The mixture was filtered in a wood filter-press and the solution treated with a further small quantity of matte while air was blown through to purify the solution from iron, arsenic, and antimony.

The air blowing can be omitted in slime treating, as the presence of ferrous iron in the solution is not an objection.

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\* Mineral Industry, Vol. 10, page 231.

One treatment of the solution with a slight excess of matte would be sufficient. The arsenic, antimony, and fluosilicic acid being removed by neutralization, the result is a neutral solution of cupric and ferrous sulphates. This requires acidification to say 2%  $\text{H}_2\text{SO}_4$ , before electrolysis, to save power.

The insoluble residue would contain considerable antimony, and if the solution contained traces of bismuth, considerable of that beside a good deal of lead and some copper. By smelting the leached matte in a lead-furnace the antimony and bismuth values would be recovered in the lead produced. On the supposition that 59 lbs. ferric iron are required to treat the slime from one ton of lead, which is a fair average, and that the matte contains 40% copper and 14% lead, the lead bullion produced by smelting the leached matte alone would contain as much as 20% antimony, and bismuth up to 16%, if bismuth is present in the slime in large quantity. This bullion could be refined for the lead content without difficulty in the usual way, and the slime treated with dilute nitric acid to make bismuth subnitrate and antimony oxide. It would probably be more advantageous to dilute the matte with lead ore before smelting to produce a purer bullion with less loss of antimony and bismuth in the furnace.

If the lead bullion only contained a little bismuth, as is usually the case, say  $\frac{1}{2}$  to 1 lb. per ton lead, the bismuth would be practically all recovered from the leached matte, in the resulting lead bullion.

**Perfluoride processes.**—Antimony pentafluoride, and also ferric sulphate with the addition of HF amounting to the use of ferric fluoride, have been tried. The ferric sulphate

and HF process possesses the advantage over the ferric sulphate process, that the antimony goes into solution with the copper and arsenic. At the time the experiments were made, I was trying to dissolve silver with the copper, arsenic, etc. Silver is not dissolved nearly as well in presence of HF by ferric sulphate as without HF. The experiments were given up on account of the inability of dissolving silver, but if this was not required, and it was possible to separate the arsenic by crystallization as  $\text{As}_2\text{O}_3$ , and a diaphragm cell, unattackable by HF, could be provided for electrolyzing the solutions, the process would be workable as well as simple and quick. The operations ought to be treatment of slime with solution of copper, antimony, and arsenic. Insoluble residue consists of lead sulphate, silver, gold, and bismuth fluoride. In solution, ferrous sulphate, cupric sulphate, antimony trifluoride and arsenious acid, .01-.02% bismuth, and stannic fluoride, in case slime contains tin.

The solution would then be electrolyzed with antimony anodes and copper cathodes, with a current density of 3-5 amperes per square foot until nearly all copper was deposited out. Then a short electrolysis with antimony anodes and copper cathodes in a separate cell would remove the remaining copper with some antimony. The solution would then be electrolyzed for the metallic antimony and the regeneration of the ferric salt, and cooled at some stage of the process to crystallize out  $\text{As}_2\text{O}_3$  if possible.

The slime treated contained Ag 29.2%; Cu 7.1%; Pb 10.2%; Sb 30.5%; As 6.10%; O 6%;  $\text{H}_2\text{O}$  not determined.

Some of the results are given in Table 47.



TABLE 47.

Slime.	HF.	H <sub>2</sub> SO <sub>4</sub> .	Fe'''.	Temperature.	Volume.	Ag Dissolved.	Fe''' Excess.
100 gr. 50 gr.	30 gr. 15 gr.	200 gr. 85 gr.	130 gr. 30 gr.	Hot ....	4000cc. 700 cc.	10.5 None	75

The filtrate from the second treatment was boiled up with fresh slime to throw out copper and arsenic, and electrolyzed with lead cathode, C.D. 9–18 amps. per square foot, and lead anode C.D. 54–108 amps. per square foot. The antimony deposited contained 1.62% Cu and 5.85% Pb (from cathode).

The process was varied by treating unoxidized slime, with ferric fluoride and sulphuric acid, in quantity sufficient to extract antimony, and then with ferric sulphate alone to extract copper.

The slime had the same analysis as the above, but was reduced by treatment with lead and fluosilicic acid to get it back to its original metallic condition as nearly as possible. The first solution contained in 3240 cc. 76 grams Fe''', 125 gr. HF, 100 gr. H<sub>2</sub>SO<sub>4</sub>. Solution after the reaction contained Cu 4.68 grs.; Sb 47.35 grs.; As 8.02 grs. On standing in a lead pan all the copper deposited out, as well as a small amount of antimony on the lead.

The second solution applied to the slime contained in 2800 cc. 110 grs. Fe''' and 150 gr. H<sub>2</sub>SO<sub>4</sub>. After reaction, the solution contained 47.25 grams of silver, precipitated out by metallic copper, while 41 grams copper dissolved. The solution then contained Ag, none; Cu, 50.9 gr.; Sb, 2.14 gr.; As, 3.12 gr. The residue contained PbSO<sub>4</sub>, 63.5%; Pb, 2.42%; Cu, none; Sb, 6.24%; As, .5%.

The results are given in Table 48.

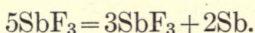
TABLE 48.

	In Slime.	In Fluoride Solution.	In Sulphate Solution.	In Residue.
Silver.....	58.4 grs.	.....	47.25 gr.	
Copper.....	14.2 grs.	4.68	10.30 gr.	None
Arsenic.....	12.2 grs.	8.02	3.25 gr.	.49 gr.
Antimony.....	61.0 grs.	47.35	2.23 gr.	6.17 gr.
Lead.....	20.4 grs.	.....	.....	45 gr.

The electrolysis was intended to be carried out as follows: The fluoride solution was to be electrolyzed for ferric fluoride and antimony, and the sulphate solution for ferric sulphate and copper.

**Antimony pentafluoride.**—This process is intended to dissolve everything from the slime except gold, lead, and bismuth, the last two of which are insoluble. Antimony pentafluoride was thought to be a stronger oxidizer than ferric fluoride.

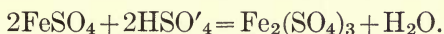
I electrolyzed antimony trifluoride solution containing about 14% Sb as  $\text{SbF}_3$ , freed from  $\text{H}_2\text{SiF}_6$  by adding KF, to precipitate  $\text{K}_2\text{SiF}_6$ , with a graphite anode and lead cathode, separated by cotton cloth. The e.m.f. required to carry out the reaction,



is about 1.45. The polarization was about .2 volt. The current density in my experiment varied from 21 to 40 amperes per square foot on cathodes, and a little less on anodes, with an e.m.f. with the latter current density of 2.35 volts. The process is not a success because frequently it is difficult to reduce the  $\text{SbF}_5$  formed, and its action on slime is far too slow.

**Ferric salts of strong monobasic acids as oxidizers.**—Ferric acetate was tried and found to be valueless. On the other hand, with strong acids (see page 19), especially methyl sulphuric acid (for the preparation of which see Chapter IV), dissolves from the slime at one treatment, bismuth, copper, arsenic, and lead, leaving silver, gold, and antimony trioxide. HF precipitates insoluble bismuth fluoride from the solution, copper is precipitable by lead, and the solution of ferrous and lead methyl sulphates may be electrolyzed for ferric salt and lead. In distinction to ferrous sulphate (polybasic acid), ferrous methyl sulphate is easily oxidized with a carbon anode at the ordinary temperature, even though the anode is not moving. The difference is probably due to difference of valency.

The reaction  $\text{Fe}(\text{SO}_4\text{CH}_3)_2 + \text{SO}_4\text{CH}_3' = \text{Fe}(\text{SO}_4\text{CH}_3)_3$  is a simpler reaction than



In the first case the anion reacts with a molecule present in large quantity, while in the second case the reaction requires the molecular connection or contact of four different parts, which can readily be conceived to occur less often.

**Use of lead peroxide as oxidizing agent for slime.**—If lead fluosilicate solution is electrolyzed with a carbon anode and a lead cathode a solid smooth coating of  $\text{PbO}_2$  is deposited on the anode, and if the solution contains gelatine a smooth deposit of lead is deposited on the cathode. The lead peroxide in its massive form is quite inactive, but if ground fine and mixed with raw slime in the presence of fluosilicic acid the metals of the slime will be oxidized into solution.



Lead peroxide was mixed with slime and lead fluosilicate—fluosilicic acid electrolyte for the purpose of extracting lead, copper and silver and leaving a residue of antimony trioxide and gold. The results were not satisfactory either in point of time required or in extraction of metals.

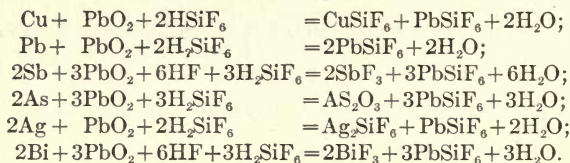
Later experiments showed the possibility of having sufficient HF present to take all the antimony into solution along with the other metals. A solution of lead fluosilicate containing, for example, 5–6% lead and 15%  $\text{SiF}_6$ , permits of the addition to it in the cold of about 5% anhydrous HF without causing a precipitation of lead, and at a higher temperature considerably more may be added. The explanation of this is that fluosilicic acid is a considerably stronger acid than hydrofluoric acid and is capable of decomposing insoluble lead fluoride until the percentage of hydrofluoric acid becomes great enough to precipitate lead fluoride and a condition of equilibrium is reached. On the other hand a solution of antimony trifluoride may be added in any quantity to the lead fluosilicate solution, without causing precipitation of lead fluoride, consequently it is feasible to take the antimony into solution simultaneously with lead, by having a certain amount of hydrofluoric acid present. Furthermore, the recovery of antimony from a mixed solution of antimony fluoride and lead fluosilicate can be nicely carried out by electrolysis with a lead anode and a carbon cathode. Antimony deposits on the cathode and lead fluosilicate dissolves on the anode until the percentage of hydrofluoric acid in the solution becomes quite high, and thereafter lead precipitates as  $\text{PF}_2$  in the neighborhood of the anode. On these principles I thought a good slime process could be based, but the experiments have not been entirely successful so far, presum-

ably on account of the formation of antimony pentafluoride, from the reaction of lead peroxide and antimony fluoride. At any rate the antimony goes into solution from the slime in an irreducible form.

Thirty-three gr. air-oxidized Trail slime containing about 15.8% Ag; 8.2% Cu; 16.0% Pb; 26.0% Sb; 5.96% As, was treated with 150 cc.  $\text{H}_2\text{SiF}_6$  and 17 cc. of 50% HF, and 50 cc. of water, and 25 gr. finely-ground electrolytic  $\text{PbO}_2$  added. The solution warmed up quite a little when  $\text{PbO}_2$  was added, showing a rapid reaction. About half the silver went into solution with practically all of the other metals, except some arsenic. Had the slime not been air-oxidized much more  $\text{PbO}_2$  would have been required.

Silver was removed by precipitation with copper, and the solution electrolyzed with a carbon anode and copper cathode, for recovery of  $\text{PbO}_2$ , and metal. Until most of the copper had been removed, a good copper deposit was obtained. Then the cathode darkened and eventually the deposit evidently consisted of lead. It contained no antimony, showing the presence of an antimony compound widely differing from the ordinary variety.

In another experiment unoxidized specially prepared slime, containing on dry sample Ag 4.5%; Bi 1.1%; Cu 17.4%; Sb 38.0%; As 12.0%; Pb 11.0%, was treated with lead electrolyte containing about 4% Pb and 20–25% SiF. The solution had been prepared by the electrolysis of a solution high in lead and containing some HF, though not enough to precipitate lead at any time. This amount of HF was sufficient for the experiment, so none was added. On adding the finely-ground  $\text{PbO}_2$  necessary for the reactions given below the temperature rose rapidly.



The actual increase of temperature was  $15^\circ$ , while the energy of the reaction was about equivalent to a change of temperature, allowing something for the box, of about  $26^\circ$ , so the reactions actually taking place only amounted to 57.5% of the total energy expected. At the time this was thought to be on account of not entirely completed reaction, which is no doubt the case to a considerable extent, but the formation of an antimony or arsenic compound of higher valence is also probable. The residue consisted of 30% by weight of the original dry weight.

By heating the residue to a high temperature with the solution further reactions took place, with the solution of some of the slime, and reduction of the solution.

The advantages of the process would be important, mentioning:

(1) The slime need not be washed or even removed from the electrolytic tanks, as the slime solution and lead refining solutions are the same, and the excess accumulating in the slime plant, derived from the electrolyte contained in the slime treated, would be returned, after proper purification.

(2) The metals are directly recovered by electrolysis in a good state of purity.

(3) The electrolytic tanks are of the simplest kind, no diaphragms being necessary.

The chief disadvantages would be the necessity of collecting a good deal of  $\text{PbO}_2$  and grinding it, and the necessity



shown to exist of working the slime treatment at a high temperature.

The electrolytic deposits obtained would consist first of copper and then of an alloy of copper and antimony, then of antimony, then of impure lead containing mostly arsenic and some antimony. The intermediate products may be refined in the same solution, using the impure cathode as anode in a separate cell through which the solution passes at the appropriate stage of its progress through the tanks. For instance, the antimony copper alloy deposited intermediately between pure copper and rather pure antimony, would be refined in the solution which contains copper as it first comes to the electrolytic tanks. In this way the impure cathodes would not accumulate, but a certain quantity would always be on hand in the course of working up into pure metal. In the example given the copper and antimony of the alloy dissolve at the anode, while only copper deposits at the cathode and the antimony accumulates in the solution. The power consumption per ton of bullion of an ordinary quality, containing say 1% antimony,  $\frac{1}{2}$ % each copper and silver, and  $\frac{3}{16}$ % arsenic would amount to about 45 K.W. hours, which is very moderate. In fact the power requirement is less than in any other electrolytic slime process discussed so far.

**Alkaline regeneration processes.**—Alkaline solutions containing sulphides are the only ones that will dissolve much from the slime. Hypochlorite solutions were tried, and arsenic was removed quite well, but it had not much action on anything else. Unsuccessful preliminary trials were also made with hyposulphite solutions also containing tetrathionate.

Slime suspended in sodium sulphide and air drawn through gives up the antimony and arsenic readily.\* Air oxidation is much more efficient with an alkaline solution or a solution of a monobasic acid as HCl, than with the customary sulphuric acid. Since the heat of combination of sulphur (liberated by oxygen and dissolved in the solution) with antimony and arsenic to form sulphosalts is probably greater than that with copper and silver, it would be expected that a good extraction of antimony and arsenic could be obtained without forming much silver and copper sulphides, though the lead would probably be converted to sulphide.

The electrolysis of sulphantimonite solutions is described by Borchers.† The yield of antimony is quantitative on amount present but not on current used. The anode reactions were the liberation of sulphur which combined to form polysulphides, and the formation of sodium hyposulphite. The polysulphide would be of immediate use as solvent for antimony in a following slime treatment, but the formation of  $\text{Na}_2\text{S}_2\text{O}_3$  represents at least a temporary loss. The percentage of the current employed in the most desirable reaction for our purpose, namely,

(1)  $\text{Sb}_2\text{S}_3 + 3\text{Na}_2\text{S} = 2\text{Sb} + 3\text{Na}_2\text{S}_2$  is calculated from Borchers's figures to be 35.8% in both cases given, and that employed in the reaction.

(2)  $4\text{Sb}_2\text{S}_3 + 9\text{H}_2\text{O} + 12\text{Na}_2\text{S} = 8\text{Sb} + 3\text{Na}_2\text{S}_2\text{O}_3 + 18\text{NaSH}$  figures 80% or over in the first case, and in the second case, about 80%. This shows that some hydrogen was liberated on the cathodes in place of antimony, as in fact must have been the case, to get *all* the antimony out.

\* Results at Trail show arsenic to be mostly insoluble.

† Electric Smelting and Refining. Second Eng. Ed., page 476.

The relative proportion of the most desirable reaction (1) and the undesirable reaction (2) is shown to be about 31% and 69% of the total.

What to do with the arsenic accumulating in the solution is another question to be considered. The current efficiency in depositing antimony is evidently rather low, unless diaphragms are used.\* A diaphragm of asbestos, supported between perforated iron plates, would be analogous to the same construction using lead instead of iron, which is entirely satisfactory in ferric sulphate electrolysis.

The conversion of thiosulphate back to sulphide could be effected by evaporating to dryness and igniting with carbon, removing oxygen and water from the mixture of  $\text{NaSH}$ ,  $\text{Na}_2\text{S}_2$ ,  $\text{NaOH}$ , and  $\text{Na}_2\text{S}_2\text{O}_3$ .

That no great difficulty would be met in treating the insoluble portion of the slime, even if converted to sulphide, by fusing to matte and heating the ground matte with concentrated sulphuric acid, is evident from the description given on page 78.

**Treatment with copper fluosilicate.**—As copper stands below arsenic, antimony, bismuth, and lead in the e.m.f. series for fluosilicate solutions, it was thought that treatment of slime with copper fluosilicate solution containing some  $\text{HF}$  would result in the solution of the above metals with a precipitation of the corresponding amount of copper, while the residue would be treated for copper and silver by refining, and the solution for arsenic, antimony, lead and bismuth in the same manner as described on page 135. No

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\* About 40% efficiency at Trail.



reaction takes place, however. The addition of HF does not help the result.

**Compression of slime to an anode plate for direct electrolysis.**—In many ways this seems the most logical method of all. We then have merely a complicated electrolytic refining operation to conduct. This it is, however, possible to do. The appropriate solution to begin with, is a solution of copper fluosilicate, fluosilicic and a few percent of hydrofluoric acid. At the anode lead, arsenic, antimony, bismuth, and copper dissolve, while copper deposits on the cathode. Fresh copper solution is continuously required, while a solution containing lead, arsenic, antimony, and a little bismuth and copper is produced. This can be worked up to the stage of containing only a little antimony and arsenic beside very much lead, in the same manner as described on pages 136 and 137.

The remaining step is the electrolysis of the solution with a lead cathode and copper anode in an electrolytic cell, with a diaphragm for the production of lead on the cathode and copper fluosilicate solution at the anode. This can also be done in a gravity cell with a horizontal lead cathode above and copper anode underneath.

**Oxidizing slime suspended in solution by air-blast.**—At Trail the first method of slime treatment consisted in blowing air through the slime suspended in  $H_2SO_4$  and salt in a lead-lined tank. This extracted the antimony and arsenic in the course of two or three days, when the antimony was to be precipitated out by diluting with water. The antimony dissolved, but the process had to be given up because no suitable apparatus for melting the insoluble portion of the slime was available. The melting was attempted in cru-

cibles, which were rapidly corroded by the basic fluxes used, and the capacity of the whole arrangement was too small. Also the cost of sulphuric acid and salt was quite a heavy item. Laboratory tests had showed an extraction of the antimony in about three days, and considerable confidence was unfortunately placed in the current statement in books that blowing air through slime suspended in sulphuric acid was an efficient means of oxidation. The long time required in the laboratory test was thought to be due to the small scale of operation and shallowness of the layer through which the air passed. This process is, however, available when salt and sulphuric acid are cheap and enough tank capacity is at hand.

Air oxidation with sulphuric acid is probably considerably slower yet. The presence of iron salts, which are converted by air from the ferrous condition to ferric condition, might be thought to be an aid to the process, but the oxidation of acid ferrous sulphate solution for example, by air, is extremely slow. I thought at one time that if ferric sulphate could be made in this way and then used to attack slime it could be used over and over again, crystallizing out copper and arsenic occasionally and adding sulphuric acid to make up for that removed by copper. Various arrangements were tried unsuccessfully, including the use of platinum black as catalyzer.

The necessary oxidation of the iron can, however, be easily secured in another way. The solution of ferrous sulphate, resulting from the treatment of slime, which solution should be as hot and strong as possible, was cooled when ferrous sulphate crystallized out. The crystals were then gently dried and roasted, effecting a ready oxidation to basic

ferric sulphate, without loss of sulphur oxides. The product of basic ferric sulphate was completely soluble in the solution.

**Roasting processes.**—There are two classes of roasting processes for preparing slime for further treatment, one consisting in roasting the slime by itself, and one with the addition of sulphuric acid.\* Roasted by itself most slime ignites as soon as it is dry, large amounts of arsenic fume escaping and a yellow product resulting, which is largely unattacked by acid solutions, even hydrofluoric acid. The antimony appears to be converted to a higher oxide, which resists all attempts to dissolve it, and the only further treatment available is by melting. Starting with slime, however, previously rather well oxidized by drying or standing in the air, a more moderate reaction with air occurs and a less refractory product results. Even in this case the proportion of antimony soluble in HF as  $\text{SbF}_3$  approximates only say 60%. The peroxidized antimony is not appreciably reducible by boiling with acid ferrous sulphate solution.

Some slime can, however, be successfully oxidized by drying and heating at a moderate temperature, say 100–150°. The oxidation is not quite complete. The slime is next treated with hot dilute sulphuric acid and sodium nitrate added in sufficient quantity to complete the oxidation. Copper and arsenic are thereby extracted, and the residue after washing is leached with hydrofluoric acid for antimony-fluoride. The drying and heating is effected in long iron or lead pans heated by steam coils underneath for twenty-four to forty-eight hours. The slime is spread on in a layer about 4"

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\* E. F. Kern, U. S. Patent 803,601. Nov. 7, 1905.



thick, in a lumpy condition, as removed from the filter. The extraction of the copper and arsenic is best effected in a lead-lined tank fitted with stirring gear. Filtration may be either done in a press, or on horizontal cloth filters with or without vacuum underneath. Quick filtration is the best, because no great cooling takes place, with consequent crystallization of arsenious acid or salts. On cooling the solution deposits a little antimony trioxide, and arsenious acid may crystallize out, if its concentration is high enough.

The extraction of the antimony and treatment of the solution is the same as described on page 97.

**Roasting with sulphuric-acid process.**—This is a simple, effective, and convenient method of oxidation. The first step is to mix the slime with concentrated sulphuric acid, which may be done without drying the slime. The slime, however, will either be dry, or be in a cake from some kind of filter. The pasty or muddy mixture is then dried out on a plate or in a furnace with free air access. If sufficient sulphuric acid is used to form lead, silver, copper, bismuth, and antimony sulphates, the product is mostly easily treated later, probably because the antimony sulphate, as soon as it touches water, decomposes and leaves a soft residue, whereas with less sulphuric acid present lumps are produced that are with difficulty completely attacked by the solutions. Dr. Valentine has suggested air-drying first, followed by roasting with sulphuric acid, as saving acid.\*

In either case acid fumes escape from the mixture on adding  $\text{H}_2\text{SO}_4$ , which are probably fumes of  $\text{H}_2\text{SiF}_6$ , or possibly  $\text{SiF}_4$ . The smell of the fume does not suggest HF.

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\* Letter from Dr. Wm. Valentine.



During the heating the sulphuric acid carbonizes organic matter, a product of the glue added to the lead-depositing electrolyte, and in some cases has produced a product containing probably carbon in such form as to give the slime a greasy flotation. This is probably the result of the use of insufficient  $\text{H}_2\text{SO}_4$ . As a general average 1 lb. of slime will require  $\frac{6}{10}$  to  $\frac{3}{4}$  lb. sulphuric acid.

A temperature of 200–250° C. for the roasting, which only takes about two hours with a layer  $\frac{3}{8}$  inch thick, is about right. As an excess of sulphuric acid is present the product is never a dry, dusty mass, and no dusting has ever been observed. The color of the product properly roasted is purplish gray and it consists of silver, lead, copper, and antimony sulphates and gold and sulphuric acid. In what condition the arsenic is is not known, but it is probably  $\text{As}_2\text{O}_3$ . Some small amount of arsenic is probably volatilized, but the quantity lost is certainly small.

The destruction of gelatine left from the lead-depositing solution by the hot sulphuric acid is an advantage, for the resulting solutions settle and filter with greater ease than is the case with other wet methods.

The product need not be ground if sufficient sulphuric acid has been used. It is boiled up with water, using sufficient to dissolve the arsenic present. For this purpose not less than 15 parts water should be added for each part of arsenic known to be present. Considerable silver dissolves, but only from one-third to one-half of the total, so no attempt is made to separate the silver, but copper is suspended in the hot mixture until silver has been removed from the solution. In the filtrate is practically all the copper, 80 to 90% of the arsenic, and about 2.5 grams antimony,

and 2 grams bismuth per litre, if bismuth is present in the slime.

Several methods of treating the solution for arsenic, copper, and bismuth may be adopted, as crystallization for copper sulphate and arsenious acid, precipitation of copper by scrap iron or electrolysis of the solution with a lead anode for electrolytic copper, and an arsenious solution, from which  $\text{As}_2\text{O}_3$ , mixed with some  $\text{Sb}_2\text{O}_3$ , may be crystallized. The  $\text{As}_2\text{O}_3$  may be further refined by sublimation or by crystallization from hot water, to which a little HF is added to keep antimony in solution.

The first method will probably not easily yield copper sulphate free from arsenic, and I have not attempted it. The second method has been in use in practical work, but the copper only comes down slowly on scrap iron, the process is wasteful of iron and acid, and the product is a low-grade one. With the third method the cost of electrolytic precipitation as pure copper is less, the product is a finished one, and there is no loss of acid, and the separation from arsenic is nearly complete. The sulphuric acid may also be used over again, after concentration.

In one experiment the conditions were as follows: Copper volume percentage on start 3.5%, on finish 0.53%. Cathode current density 18 to 9 amperes, and even as low as 4.5 for a short time. Volts 2.3 to 2.1. Copper deposited at finish, good color. Anode of lead from one-quarter size of cathode most of the time, to same size as cathode. Current efficiency approximately 100%, but not accurately determined. A good agitation was maintained, but about the middle of the run, with current density 20 amperes, deposit got black on top for a short time.



The solution from which copper was removed was evaporated down until  $\text{As}_2\text{O}_3$  began to crystallize out, when arsenic was mostly removed in hard, glittering crystals intermixed with  $\text{Sb}_2\text{O}_3$  and some copper sulphate, which was washed out with water.

A better procedure might be to cool the hot acid solution filtered from the slime, crystallize out copper sulphate and arsenious acid, and dissolve the copper sulphate from the product with water or with similar solution from a previous treatment from which the copper has been largely removed by electrolysis, leaving the crude arsenic insoluble. Any bismuth present in the hot solution from the filter, remains in solution, as bismuth is as soluble or more soluble cold than hot, except in very strong acid. On evaporating the mother liquor down for crude sulphuric acid for the treatment of another lot of slime, bismuth and remaining copper sulphate mostly separate, or can be separated by cooling the strong sulphuric acid.

The solubility of bismuth sulphate in sulphuric acid of various strengths is approximately as given in Table 49, from experiments by Dr. E. F. Kern:

TABLE 49.

97%	$\text{H}_2\text{SO}_4$	.69	grams Bi per	100 cc. cold.
55%	$\text{H}_2\text{SO}_4$	.61	" " "	100 " "
16.6%	$\text{H}_2\text{SO}_4$	.19	" " "	100 " "
10%	$\text{H}_2\text{SO}_4$	.22	" " "	100 " "
10%	$\text{H}_2\text{SO}_4$	.21	" " "	100 " "
3%	$\text{H}_2\text{SO}_4$	.16	" " "	100 " "
4%	$\text{H}_2\text{SO}_4$	.10	" " "	100 " "

In general bismuth is more soluble cold than hot in weaker solutions. Thus with 20%  $\text{H}_2\text{SO}_4$  the solubility is

greater cold; with 50%  $\text{H}_2\text{SO}_4$  and stronger acids, the solubility is greater hot.

32% $\text{H}_2\text{SO}_4$	100° C.	.65 gr. Bi per 100 cc.
88%    "    "	100° C.	1.86   "   "   "   100   "

With relatively very small amounts of bismuth present most of it will be removed from the slime with the copper and arsenic. With large amounts of bismuth most will remain in the slime throughout.

The extraction with HF for antimony proceeds as described under heading "Ferric Sulphate Process", page 97, but gives even cleaner extraction in this case. Some silver dissolves, which is readily precipitated out with metallic antimony. The following figures are for Trail slime treated experimentally. The figures in the second column are not exactly right, probably partly on account of absorption of moisture since the analysis was made.

TABLE 50.

	Slime 100 Grams.	First Residue 74 Grams.	Second Residue 33.8 Grams.
Silver.....	14.6%	12.3%	20.9%
Gold ..	34.5 ozs.	.....	.....
Copper.....	8.1%	Tr.	None.
Lead.....	16%	.....	.....
Arsenic.....	7.0%	1.66%	None.
Antimony.....	27.60%	35.9%	0.56%
Bismuth.....	0.81%	.....	.....

The amounts of metals in the various products are given below. The discrepancy in silver is due to the fact that in this experiment the silver, instead of being precipitated back into the slime as would be done in practice, was precipitated

separately in the filtrate in order to determine the quantity in solution.

TABLE 51.

In Slime.	In First Residue.	In Second Residue.
14.6 gr. silver	9.1 gr. silver	7.1 gr. silver
8.1 gr. copper	No copper	No copper.
16.0 gr. lead	16 gr. lead	16 gr. lead.
7.0 gr. arsenic	1.23 gr. arsenic	No arsenic.
27.6 gr. antimony	26.6 gr. antimony	.19 gr. antimony.

The extraction of copper by the first solution was about 100%, of arsenic 80%, of antimony (from other facts), 2.6%. The extraction of arsenic by the HF is the remaining 20% of the arsenic, and of the antimony about 96.6% of the total originally present. The result in respect to antimony is superior to that obtained by the ferric sulphate method on dried slime.

In another experiment with 600 gr. lots of the same slime, the following results are given, arranged as Table 52 (p. 135) for the sake of brevity.

**Dissolving air-dried slime in  $\text{H}_2\text{SiF}_6$  and HF.**—Practically all the slime, if sufficiently well oxidized, dissolves in a solution containing both fluosilicic acid, and a moderate quantity of hydrofluoric acid, in a few hours. Lumps disintegrate of themselves. The solution resulting contains lead and copper fluosilicates, antimony fluoride, and arsenious acid. For the recovery of the various metals experimentally, the solution was electrolyzed first with an antimony anode and copper cathode, current density 2 amperes per square foot, e.m.f. .25 volts. Good copper comes down, if the solution is stirred until copper is nearly all gone, when the deposit



TABLE 52.

	Experiment 1.	Experiment 2.
Slime taken. ....	600 gr.	600 gr.
H <sub>2</sub> SO <sub>4</sub> taken calculated to H <sub>2</sub> SO <sub>4</sub> . ....	450 gr.	400 gr.
Sulphuric acid lost in roasting percent- age of slime taken. ....	33%	22%
Copper removed from solution. ....	By electrolysis	By electrolysis
Anode. ....	Lead	Lead
Copper in solution on start. ....	24 gr. per litre	21 gr. per litre
Copper in solution on finish. ....	4.0 gr. " "	2.3 gr. " "
Quality of copper with hot solution. ....	Varied	Good
Water used in dissolving sulphates. ....	5 times weight of slime	5 times weight of slime
Amperes per sq. ft. in copper deposition maximum. ....	26	9.3
Amperes per sq. ft. in copper deposition minimum. ....	9.4	2.2
Volts, maximum. ....	2.45	
" minimum. ....	2.0	
CuSO <sub>4</sub> crystallized from mother liquor. ....	18.4 gr. +	16 gr.
Copper dissolved in precipitating silver. . .	24.5 gr.	15 gr.
Wt. dry residue after dissolving sulphates	462 gr.	
Antimony dissolved to remove Ag from fluoride solution. ....	7 gr.	12 gr.
Antimony deposited. ....	114 gr.	149 gr.
Quality. ....	Fair, contained copper not thoroughly washed out before treat- ment with HF	Excellent, no copper
Arsenic in electrolyte. ....	0.3%	0.6%
Amperes per sq. ft. cathode surface, maxi- mum. ....	31.5	24
Amperes per sq. ft. cathode surface, mini- mum. ....	15.6	4.2
Amperes per sq. ft. cathode surface at end of electrolysis. ....	16.5	11.8
Volts at 20 amperes per sq. ft. ....	2.78	3.05
Current efficiency. ....	84.5	97.5
Antimony as trifluoride in solution on start, grams per litre. ....	91.4	108
Antimony as trifluoride in solution on finish, grams per litre. ....	7.6	6.9
Antimony as pentafluoride on finish, grams per litre. ....	.....	18.9
Free HF in solution on start, grams per litre. ....	25.0	14.0
Antimony loss in whole of two operations. .....	.....	7.5%
Insoluble residue melted with silica, giving clean doré weight. ....	88 gr.	

turns whitish. Analysis of copper product, 91.1% Cu; 4.8% Sb; .25% Bi; no As or Pb. The next product with copper cathode and antimony anode is small in amount and consists of antimony with about 10% copper.

The solution is next electrolyzed with a lead anode and copper cathode, current density 10 amperes per square foot, e.m.f. 0.2 to 0.4 volts. The antimony deposit contained 90.5% Sb, 5.6% As, no Cu. Some antimony also forms on the anode, as scale.

The current density should be diminished when antimony is reduced to 2%, to prevent lead from coming down.

The solution is then electrolyzed with lead anode and cathode. A soft deposit forms on the cathode, which can be compressed to solid metal. Analyses show, for successive products:

TABLE 53.

Pb		86.9%		N. d.
Sb	7.2%	9.2%	4.4%	Trace.
As	.6%	3.3%	19.6%	"

By reversing the current an anode slime of arsenic and antimony may be produced.

The solution is next electrolyzed with carbon anode and lead cathode for the production of  $\text{PbO}_2$  and Pb, containing arsenic and antimony and free acid to be used over again, in the treatment of another lot of slime. The operation sometimes succeeds and sometimes no  $\text{PbO}_2$  separates at the anode, for reasons not understood.

The solution at different times contained approximately as follows:

Column 1 shows the solution after filtering from slime, column 2 after removal of copper, column 3 after removal of

antimony, column 4 after removing arsenic and remaining antimony in lead, and column 5 after electrolysis for  $\text{PbO}_2$  and Pb. The  $\text{PbO}_2$  can be put with a charge of lead ore for recovery of lead.

TABLE 54.

Cu''	1.3%	0 %	0 %	0%	0 %
Sb'''	5 %	6.6%	.44%	Trace	0 %
Pb''	5.5%	5.5%	21.5 %	21.5%	5 %
$\text{SiF}_6''$	17 %	17 %	17 %	17 %	17 %
F'	3.5%	3.5%	3.5 %	3.5%	3.5%
As'''	1.1%	1.1%	.88%	Trace	0 %

Analysis of 50 parts of air-dried slime before treatment and 13.5 parts residue after treatment with the mixed electrolytes, Table 55.

TABLE 55.

Ag.....	14.6%	.....
Cu.....	8.1%	7%
Pb.....	16.0%	7.2%
Sb.....	27.6%	12.5%
As.....	7.0%	1.6%
Au.....	.....	.....

The analysis of the slime taken is not exact as it had probably absorbed water, and consequently the values may be a trifle too high.

The percentage of extraction was as follows, Table 56:

TABLE 56.

Copper.....	73%	extracted.
Lead.....	86.2%	"
Antimony.....	87.7%	"
Arsenic.....	93.8%	"
Silver.....	None	"
Gold.....	"	"



### CHAPTER III.

#### DEPOSITION OF ANTIMONY FROM THE FLUORIDE SOLUTION.

THE electrolytic refining of antimony with an electrolyte containing  $\text{SbF}_3$  and  $\text{HF}$ , and perhaps  $\text{KF}$  or  $\text{NaF}$  in addition,\* is a successful method, as far as the quiet solution of the anode and good mechanical quality of the cathode is concerned. The addition of  $\text{KF}$  or  $\text{NaF}$  is made to increase the conductivity of the solution. Dilute hydrofluoric acid is not as good a conductor as the other common acids, sulphuric acid for example.  $\text{KF}$  also removes  $\text{H}_2\text{SiF}_6$  from the solution as a precipitate of  $\text{K}_2\text{SiF}_6$ . It has been proved\* that the presence of sulphuric acid or sulphates in the *refining* electrolyte (to be distinguished from the electrolyte when insoluble anodes are used, as described later) prevents the easy solution of the anodes, which is readily explained by the ionic electrochemical theory, as follows: The anion  $\text{SO}_4$ , with a smaller quantity of the anions  $\text{F}'$  or  $\text{F}''_2$  whichever is produced by the dissociation of  $\text{HF}$ , combine with the anode metal to form antimony sulphate and antimony fluoride. Antimony sulphate is almost immediately decomposed into insoluble antimony oxide or hydroxide and sulphuric acid, thus leaving an insulating coating on the anode, which is only slowly, and in fact too slowly, dissolved off by free  $\text{HF}$  which may be present.

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\* Betts Trans. Am. Electrochemical Society, Vol. VIII, page 190.

This insulating coating actually exists, and may produce a local resistance sufficient to absorb .2 volt or more. As the difference of e.m.f. of solution of copper and antimony in the fluoride solution is probably considerably less than .1 volt, only a slight voltage drop is necessary to make any copper present dissolve too, and once dissolved, it readily deposits on the cathode with the antimony.

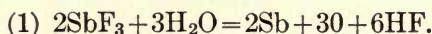
Whether copper can be left as anode slime, in absence of  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SiF}_6$ , etc., and antimony free from copper can be produced in this way, has not been definitely settled.

Arsenic probably dissolves even more readily than antimony and collects in the solution, though some will be found in the cathode metal under some conditions, if not all.

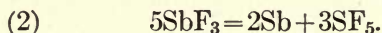
Lead is eliminated satisfactorily, provided suitable cathodes of other material than lead are used.

Antimony trifluoride is an extremely soluble salt. Its cold saturated solution in water has a specific gravity of about 2.6 and contains about three parts  $\text{SbF}_3$  to 1 part  $\text{H}_2\text{O}$ . By adding other salts as sodium, ammonium, potassium, chlorides, fluorides and sulphates, double salts of less solubility may be secured. Antimony trifluoride is used as a mordant in dyeing, though probably better results are got with antimony lactate and tartar emetic.

The deposition of antimony from the trifluoride solution, which in this case may well contain  $\text{H}_2\text{SO}_4$  or sulphates, is important in working up anode slime, as it is often convenient to dissolve the antimony oxide in oxidized slime, or slags from melting slime in dilute hydrofluoric acid, followed by deposition of the antimony from the solution. With an insoluble anode the principal reaction is



There is a secondary reaction that takes place, namely,



The last reaction is undesirable, as the antimony in  $\text{SbF}_5$  represents a loss of both antimony and fluorine as the process is worked at present. It is hoped to devise means to reduce this  $\text{SbF}_5$  again to  $\text{SbF}_3$ , but no serious attempt has been made yet.

Reaction 2 is favored by high percentage of  $\text{SbF}_3$ , high temperature, low percentage of  $\text{H}_2\text{SO}_4$ , large anode surface, and ready access of solution to the anode surface, so the opposite conditions are adhered to in practice, when reaction 2 may be reduced to about 5% of the whole electrochemical effect.

The available anode materials are platinum, carbon, and lead. It is quite possible that fine platinum wires would make an excellent and permanent anode, but they have not been tried. Carbon anodes of all kinds distintergrate rapidly, and can only be used when the solution is supplied with some reducing agent, as  $\text{SO}_2$ . This is of course converted at the anodes into  $\text{H}_2\text{SO}_4$ , and might be used practically, except that it is also reduced at the cathode, forming  $\text{Sb}_2\text{S}_3$ . Lead anodes only are actually used, but it is necessary to use them in a special manner, both to save lead, and to prevent the formation of much  $\text{SbF}_5$ .

The commercial hydrofluoric acid used in extracting antimony from slime and slags from melting slime, contains  $\text{H}_2\text{SiF}_6$ , and as the slime or slag usually contains silica, further quantities of  $\text{H}_2\text{SiF}_6$  are formed. Dr. Wm. Valentine has noticed that in making HF by distilling fluorspar with sul-



phuric acid, the first HF to come off contains most or all of the silica, and has suggested using the first part in making lead refining electrolyte and the last in slime treating.

The presence of fluosilicic acid (or any acid forming a soluble lead salt) is undesirable, for it acts on the lead anodes as a strong "forming" agent, and therefore reduces the life of the anodes.  $\text{H}_2\text{SiF}_6$  is usually removed sufficiently by precipitation with sodium sulphate. Potassium sulphate is better, but its cost has been too high. However, as the

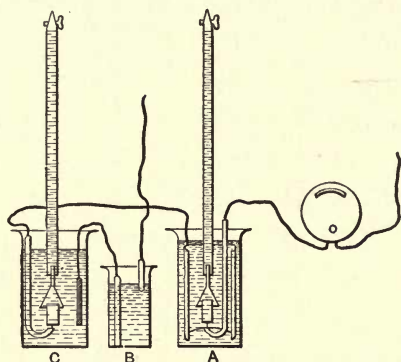


FIG. 21a.

sodium fluosilicate is too valuable to throw away, and should be distilled with  $\text{H}_2\text{SO}_4$  and a little fluorspar anyway, to recover the  $\text{H}_2\text{SiF}_6$ , potassium sulphate would be equally as economical, for the residual potassium sulphate could be used over again.

To test the anode reactions, antimony trifluoride solution containing also ferrous sulphate, to imitate conditions in practice when iron gradually accumulates in the solution, was electrolyzed in series with a gas voltameter, provisions being made for collecting the gas liberated at the anode.

Apparatus as shown in Fig. 21a was used. A is a gas

voltameter using lead anode and cathode in an acid solution of copper sulphate. *B* is a resistance cell for regulating the current. *C* contains the electrolyte under investigation and has a small lead anode from which the escaping gas can be collected and measured in the burette. The results are tabulated in Table 57.

TABLE 57.

No.	Amperes per Square Foot of Anode.	Average Voltage.	Percentage of Current Used in Generating Oxygen Gas.	Solution.
1	87	3.4	75.3	$\left. \begin{array}{l} 7.5 \text{ gr. SbF}_3 \\ 5 \text{ gr. H}_2\text{SO}_4 \\ 25 \text{ gr. FeSO}_4 \cdot 7\text{H}_2\text{O} \end{array} \right\} \begin{array}{l} \text{per} \\ 100 \\ \text{cc.} \end{array}$
2	87	3.4	77	
3	85	3.3	81.6	
4	86	3.3	82.4	
5	88	3.2	71.5	$\left. \begin{array}{l} 15 \text{ gr. SbF}_3 \\ 40 \text{ gr. FeSO}_4 \cdot 7\text{H}_2\text{O} \\ 5 \text{ gr. H}_2\text{SO}_4 \end{array} \right\} \begin{array}{l} \text{per} \\ 100 \\ \text{cc.} \end{array}$
6	81	3.2	72.7	
7	87	3.1	72.6	
8	85	3.3	71.4	
9	75	3.2	71.7	
10	73	3.1	66.5	
11	65	2.9	65.1	
12	45	2.6	52	
13	31	2.7	42.5	

The figures given for percentage of current used in generating oxygen gas give, by subtraction from 100, the percentage of the current used in oxidizing ingredients of the solution, which is not desired. If iron is oxidized the ferric salt will react at the cathode and cut down the efficiency, and any antimony oxidized results in temporary loss of antimony.

The highest efficiency in Table 57 is surpassed in practical work with lead rods as anode, wrapped in several thicknesses of cloth to prevent the free access of oxidizable salts to the anode surface.

The accompanying Table 58 shows the efficiency in experiments in depositing antimony where the efficiency was accurately determined and other data carefully noted.

In experiment 2 in the table, no cloth was wrapped around the anode rods and the lower efficiency should be noted.

TABLE 58.

No.	Date.	Quantity Deposited.	Current measured by	Anode Current Density per Square Foot.	Cathode Current Density per Square Foot.
1	March 1905	25.7 gr.	Lead voltameter	375-60 amps.	25.4 amps.
2	Sept. 1903	1.077 kg.	Ammeter	180-120 "	22.5-15 "
3	Sept. 1903	.91 "	"	75-38 "	19-9.5 "
4	Oct. 1903	.874 "	"	100-40 "	25-10 "
5	Oct. 1903	1.243 "	"	92-52 "	23-14 "
6	Oct. 1903	1.585 "	"	105-34 "	26-8.5 "
7	March 1907	114 gr.	"	102-51 "	31.5-15.6 "
8	March 1907	149 "	"	120-21 "	24-4.2 "

No.	Date.	Efficiency.	Sb''' on Start in Solution per 100 cc.	Sb''' on Finish in Solution per 100 cc.	Volts.
1	March 1905	90.0%	3.48 gr.	0.80 gr.	3-28
2	Sept. 1903	66.5	6.8 "	1.36 "	3-2.75
3	Sept. 1903	84.5	5.52 "	1.83 "	2.9-2.7
4	Oct. 1903	92.9	5.58 "	1.83 "	3.15-2.45
5	Oct. 1903	95.4	7.33 "	2.07 "	2.9-2.55
6	Oct. 1903	92.0	8.1 "	2.15 "	2.9-2.55
7	March 1907	84.5	9.14 "	.76 "	3.05-2.78
8	March 1907	97.5	10.8 "	.69 "	

No.	Date.	Sb'''' on Finish in Solution per 100 cc.	Na <sub>2</sub> SO <sub>4</sub> per 100 cc.	H <sub>2</sub> SO <sub>4</sub> per 100 cc.	H <sub>2</sub> SiF <sub>6</sub> per 100 cc.	F' per 100 cc.
1	March 1905	.....	.....	4.66 gr.	.....	4.1 gr.
2	Sept. 1903	.....	1.5 gr.	.....	.....	4.1 "
3	Sept. 1903	.....	.24 gr.	.....	.....	4.4 "
4	Oct. 1903	.....	.....	1.1 gr.	0.8 gr.	3.2 "
5	Oct. 1903	.....	.48 gr.	.....	.....	4.5 "
6	Oct. 1903	.....	.....	.....	1. gr.	3.87 "
7	March 1907	.....	Excess	3.0 gr.	.....	7.0 "
8	March 1907	1.89* gr.	.....	.....	.....	6.45 "

\* Total amount produced in runs 7 and 8=approx. 10%.



The anodes are of soft lead rods, usually  $\frac{1}{4}$  to  $\frac{3}{8}$ " diameter, and covered with 2 to 4 layers of cotton cloth to prevent the access of much  $\text{SbF}_3$  to the actual anode surface with its oxidizing conditions. Oxygen escapes vigorously while the current is on. The anode rods are spaced about 3 inches apart in rows with cathode plates between. An experimental tank is described and illustrated on page 396, and a commercial tank on page 260.

The electrolytic antimony may be pure or not, according to the solution used. When lead cathodes are used the antimony is found to contain lead, the reason being evident to anyone who examines the corrosion of a lead cathode, when such has been used. A copper cathode is more satisfactory.

The presence of lead in the antimony is avoidable and so is that of copper. If the solution contains copper, it comes down with the first antimony deposited, it being necessary to deposit perhaps one-tenth of the total antimony to get the copper all out. In practical work, however, little or no copper is found in the solution anyway.

The removal of the copper is better carried out before the electrolysis in either one of two methods, or if the quantity is large, by a combination of the two. For considerable quantities of copper the solution is electrolyzed with antimony chunks as anode and copper cathodes. With a cathode current density of 2 amperes per square foot and anode current density, which may be as high as 10 amperes and .4 to .5 volts practically all the copper can be got out as good copper, while of course a corresponding amount of antimony goes into solution. For results with this method see Table 59.

TABLE 59.

No.	Copper on Start	On Finish.	Anode C. D. per Sq. Ft.	Cathode per Sq. Ft.	Remarks.
1	.24%	Trace	About 10	2	Contained much $\text{H}_2\text{SiF}_6$
2	.50%	"	2-8	2-8	
3	1.00%	.03	About 5	3-2	

Small quantities of copper may be conveniently removed by direct precipitation on antimony. While merely dropping some antimony into a tank containing the coppery solution does little or no good, an arrangement as shown in Fig. 21b is successful, especially if the solution passes through slowly

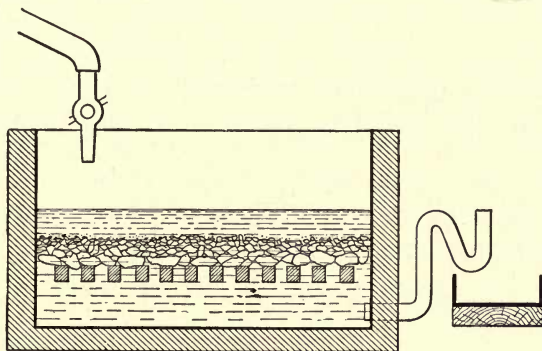


FIG. 21b.

and at a slightly raised temperature, say  $40^{\circ}\text{C}$ . The tank contains broken antimony resting on a false bottom, in a layer 4" or more thick. Copper deposits on the top of the mass, while antimony dissolves away underneath. The solution escaping has a yellowish color and probably contains traces of copper as cuprous fluoride.

The removal of arsenic is not readily accomplished before the electrolysis, and the best way seems to be to let it

accumulate in the solution, which it may be expected to do in practice at the rate of about 1 part arsenic or less dissolved for 30 parts antimony deposited (see page 98, Chapter II). Antimony deposits more readily than arsenic.

For analyses of electrolytic antimony from slime, see Table 60.

TABLE 60.

## ANALYSES OF ANTIMONY.

No.	Ag	Pb	Cu	As	Bi	Sb
1	Nil	1.6%	2.9%	2.3%	.....	93.8%
2	"	.62%	.2%	.....	.67%	.....
3	"	Nil	.07%	.41%	Nil	.....
4	"	Nil	Trace	0.5-1.00%	Nil	.....

No. 1 from solution not purified from copper used over and over in consecutive treatments and deposited on lead cathodes.

No. 2 from slime containing much Bi. No refining of solution from copper necessary in this case.

No. 3 from solution purified of copper before electrolysis. Deposited on copper cathodes.

No. 4 from commercial work. Poorer quality also produced. Arsenic is hard to keep down.

In general, the antimony deposited will contain 0.5 to 1.0% arsenic, and no easy method is known so far of producing antimony free from arsenic in this way. However, arsenic is about the easiest to remove in the dry way of the metals we consider here. Arsenic in the presence of bases is more oxidizable than antimony and can be slagged off as sodium arsenate by fusion under soda in presence of oxidizing agents.



The deposited antimony is usually solid and hard, with a jagged but bright surface. However, when antimony becomes reduced to from 1 to 2%, according to the current density, the deposit gets black and soft, probably due to arsenic coming down too, and it begins to fall from the cathodes as powder. At this point, the operation should be stopped. The deposited antimony shows a tendency to peel, but does not usually fall off the cathodes. It is easily removed from the cathodes, particularly as these are flexible and the brittle antimony separates readily on bending.

The deposit appears to contain some of the solution, as acid fumes escape on melting, and the metal loses slightly in weight.

As lead slime usually contains excess of silica, averaging perhaps 1-2% silica in addition to some fluosilicic acid or fluosilicate, when antimony is extracted with HF, some silica also dissolves, varying in amount from 0.9 to 1.8% calculated on original weight of slime. By precipitation with sodium or potassium sulphate sodium fluosilicate is produced, which can be utilized by adding it in with a charge of fluorspar in the hydrofluoric acid plant.

**Cost of depositing antimony from the fluoride solution with insoluble anodes.**—This process has not been used on a practical scale long enough for actual operating costs to be determined, but the cost can be quite closely estimated. The tanks for practical work may take 4000 amperes, at 2.8 to 3.0 volts, and are 7 feet 2 inches long, 2 feet 6 inches wide, and 3 feet 6 inches deep. Current, 15 amperes per square foot of cathode surface. Anode, 20 sets of 10 lead rods, each  $\frac{3}{8}$ " diameter.

TABLE 61.

	Per Pound Antimony.
Power cost at \$50 per E.H.P. year at 95% efficiency, 1.20 H.P. hours at \$0.00575. ....	\$0.0069
Breaking antimony from cathodes and labor cost operating tank..	0.0010
Melting antimony in crucibles and casting.....	0.0010
HF loss, mechanical, 5%.....	0.0018
HF loss from formation of $\text{H}_2\text{SiF}_6$ .....	0.0057
$\text{Na}_2\text{SO}_4$ , .12 lbs. at \$15 per ton. ....	0.0009
Labor cost, precipitating and collecting $\text{Na}_2\text{SiF}_6$ .....	0.0010
Renewals of anodes (in 7 days 3 lbs. Sb deposited per ft. anode used), Smelting and refining and squirting 0.18 lbs. lead at \$20 per ton including losses. ....	0.0018
Cloth and labor wrapping anodes. ....	0.0020
Repairs and interest. ....	0.0020
Total. ....	<u>\$0.0241</u>
Credit for $\text{Na}_2\text{SiF}_6$ , added to fluorspar in making HF, yield $\text{H}_2\text{SiF}_6$ = 80%. ....	<u>0.0040</u>
Net cost per lb. antimony deposited.. ....	<u>\$0.0201</u>

## CHAPTER IV.

### ELECTROLYTIC REFINING OF DORÉ BULLION.

THE older nitric-acid and sulphuric-acid processes are well described in various works on the metallurgy of silver and gold,\* to which the reader is referred.

The electrolytic processes are now coming largely into use, and it is doubtful if the sulphuric-acid process will be much installed in future in large works.

Further improvements in the electrolytic processes may be expected, particularly for alloys containing copper, so that the sulphuric-acid process will fall farther behind than ever. In the older parting processes it was desired to remove the base metals as fully as possible to save acids in parting and make the process more easily conducted. This was done at quite high cost, and not without losses, by cupellation and furnace treatment, and the practice is still in vogue even at plants using the electrolytic processes, because in that way there is required less renewals of the electrolytes to get rid of the accumulating base metals and keep the silver percentage at the necessary amount. However, the accumulation of base metals in the electrolyte need not necessarily be a disadvantage and in the future it will be found better to leave out the furnace refining for bullion from anode slimes, and

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\* Rose, "Metallurgy of Gold"; Eissler, "Metallurgy of Gold."



recover the base metals present from the electrolyte instead, which it is easy to do in many ways, and will permit greater economy than long and expensive furnacing with unavoidable metal losses.

The parting process of Dr. Dietzel\* is based on sound principles, which ought yet to be more largely applied in better apparatus. Alloys of gold, silver and copper, containing

Au.....	5-7%	Zn, Sn, Pb, about 5%
Ag.....	22-50%	Cd, Fe, Ni, Pt, Traces
Cu.....	40-65%	

were successfully treated on a rather small scale.

The process consists in electrolyzing a solution of copper nitrate with copper cathode and bullion anode, separated by a diaphragm, copper depositing on the cathode of course, and all the metals except gold dissolving from the anode. With alloys containing 40% silver or less I have found it difficult to dissolve any silver from hanging electrodes, as the other metals dissolve first and leave the silver as a mushy anode slime, and the same objection was probably found by Dr. Dietzel, as his apparatus has a horizontal conducting anode, of carbon probably, on which the alloy rests, and in this way of course the silver may be finally dissolved.

There is maintained a continuous flow of copper nitrate solution to the catholyte, while the anolyte containing silver overflows and runs to a precipitating tank in which the silver is cemented out by copper, and the solution then goes back to the electrolytic cell. This system has important advantages which should not be lost sight of.

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\* Borchers, "Electric Smelting and Refining," 2d Eng. Ed., page 304.

(1) The system is perfectly cyclic (except if the anodes contain iron, zinc, tin, and lead), and so little or no maintenance of solution is required.

(2) The process is not affected by variation in the composition of the anodes, as it will work the same on a series of alloys all the way from pure copper on one end to pure silver on the other.

(3) All the silver is precipitated in one or two tanks, and the superiority of this plan over collecting spongy silver from a large number of different cells is apparent.

(4) Whatever copper is present in the anodes appears as electrolytic copper.

One objection, though not readily apparent, may be noted. If selenium or tellurium, or other metal precipitable by copper dissolves from the anodes the silver will contain that element. This objection applies to most precipitation processes. Whether by a partial precipitation of the silver the selenium or tellurium could be concentrated in a small part of the silver, is not known, but it seems that this probably could be done. Under some quite usual conditions I do not believe, however, that selenium or tellurium would dissolve with the silver. These conditions are found when the anode contains a preponderating amount of silver.

With the Dietzel process it will be seen that the silver and copper solution escaping from the anode compartment might be strong enough in silver to provide electrolyte for an electrolytic silver refining cell, while the electrolyte from the latter, impoverished in silver, might then be carried through the rest of the process as originally intended. For an ordinary Moebius or analagous parting plant, the use of a number of cells on the Dietzel principle would be desirable,

as providing a means of recovering copper from and returning silver to the electrolyte.

The cell used by Dr. Dietzel does not appear to be especially well suited to the work, however. The use of rolling cylinders of copper cathodes would seem unnecessary. For most doré bullion, the percentage of silver is so high that the silver may be cast directly to anodes and suspended or supported in the solution, instead of requiring a flat surface on the bottom on which to support the pieces of doré and the slime, still containing considerable silver in that case.

A diaphragm cell with diaphragms of porous earthenware or asbestos sheets supported between perforated slate or glass plates, or asbestos plugs in holes in a wood partition, or one of hardened asbestos (see page 110) can all be expected to give a good result, of which the one objection is that silver moves under the action of the current through the diaphragm and toward the cathode, and interferes with the deposition of a solid smooth cathode. This objection (not a very serious one) can be got around by using a double diaphragm and in the space between a piece of metal, for example copper, to precipitate silver. I have tried this arrangement, but the results are not conclusive either way.

For refining bullion containing lead and bismuth apparatus as shown in Fig. 22 gives good results. The bullion is placed as anode in cell 1 with a lead cathode and a diaphragm of sulphurized asbestos between. A steady flow of lead methyl sulphate solution containing 5-6% Pb and 12-15%  $\text{CH}_3\text{SO}_4$ , is maintained to the cathode compartment in which lead is deposited in a fair condition of solidity. This lead is not pure, however, and in practice would go to the lead-bullion kettle. At the doré anode, silver, copper, bismuth, and lead



dissolve, provided the doré contains approximately 70% silver or over. If less bismuth and lead dissolve and leave a mushy anode slime of silver containing about 15% of lead and bismuth. The solution continually overflows from the cathode compartment where the percentage of lead is reduced, to the anode compartment, while solution containing silver, lead, bismuth, and traces of copper flows through a series of beakers to a storage vessel. The first two contain pieces of

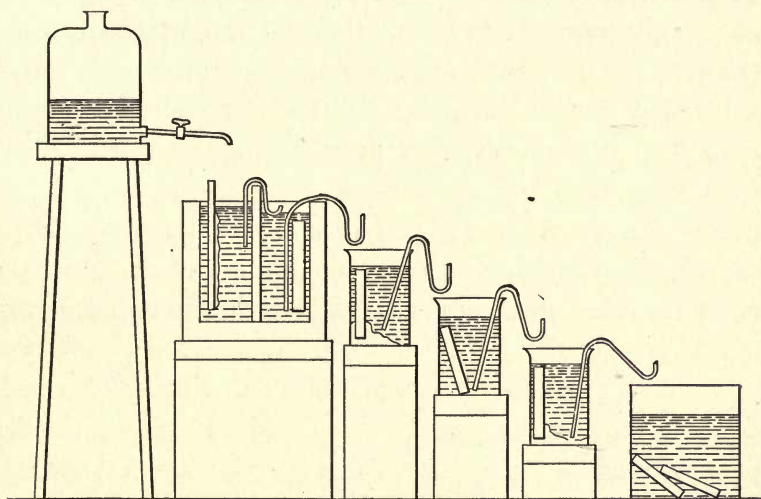


FIG. 22.

bismuth, which cement the silver out readily, and the last two contain metallic lead, which throws out the bismuth. The solution, practically free from copper and bismuth, is elevated to the higher storage tank and passes through the series again. The current density in the electrolytic cell was 15 amperes per square foot. Electromotive force, 2 volts.

A process for getting the silver into solution quickly at the anode, without introducing any difficulties at the cathode

in the way of producing a solid deposit of silver, or lead, or copper, as the case may be, is furnished by the use of lead peroxide and a solution of fluosilicic acid, for instance. The doré may be dissolved at a very high current density if the lead peroxide is used as cathode, especially if the cathode is of carbon electrolytically coated with the peroxide. There results a solution of lead, copper and silver fluosilicates that may be rapidly treated for silver by precipitation on copper, while the copper can be got out by electrolysis with lead anode and copper cathode, and next the lead can be removed and the lead peroxide used recovered by electrolysis with carbon anode and lead cathode; or equally well, if the doré contains little lead, the precipitation of copper as mentioned above may be omitted, and the solution containing copper and lead fluosilicates can be electrolyzed with a carbon anode and lead cathode for electrolytic copper and lead peroxide, the latter of course being used over again as cathode in dissolving more bullion.

In this process there is no difficulty either with the cathode deposits being spongy, or is there need to consider the diaphragm question, but another difficulty appears in that the lead peroxide deposits on carbon electrodes have not yet been dissolved off with high efficiency, some of the peroxide dropping from the electrodes to the bottom of the cell and thereby escaping action. To obviate this, a plate of bullion or a plate of graphite connected electrolytically to the peroxide cathodes might be placed on the bottom of the cell. The peroxide falling on the bottom in this case would be ultimately reduced and dissolved, though somewhat slowly.

The electrolytic refining of bullion has only been practically carried out with the sulphate and nitrate baths, mainly

the nitrate, which is in use in several large plants refining from perhaps 20,000 to 100,000 ounces per day. In either case the deposited silver comes down in a loose crystalline form. The older Moebius apparatus\* is well described and illustrated in the patent specification and in several available works.† The more recent Balbach apparatus,‡ improved by Mr. Wm. Thum, accomplishes the same result in a somewhat different manner. The following quotation and figures are from Mr. Easterbrooks' paper,§ read before the American Electrochemical Society.

"With electrolytic parting we have a choice of two distinct systems of depositing silver on the cathode, one in a loose crystalline form at a relatively high current density, as in the Balbach and Moebius methods, the other with the aid of gelatine in an adherent form at a lower current density.

"The electrolyte used is a copper-silver nitrate solution, although recently Betts || has proposed using a silver methylsulphate solution.

"These methods all have in common the characteristic of parting and refining bullion free from gold and tellurium at one operation, the deposited silver being melted and poured into bars without any further refining, as in the sulphuric acid process. Silver placed in the tanks as anodes is not handled until taken out as refined silver, whereas in the acid method the silver either in solution or as cement must be transferred several times with the aid of siphons, steam, etc., before

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\* U. S. patent 310302 and 310533. Jan. 6, 1885.

† Borchers, "Electric Smelting and Refining," 2d Eng. Ed.; Watt and Philip's "Electroplating and Electro-refining," "Mineral Industry," Vol. VIII (1889), page 337.

‡ U. S. patent 588524.

§ Trans. Am. Electrochemical Society, Vol. VIII (1905), page 131.

|| Electrochem. Industry, April, 1905.



it is in a condition to be melted. For these reasons it is possible to operate an electrolytic parting plant with a higher degree of neatness and cleanliness (such as the value of the material treated requires) than is possible with acid parting.

"A. parting plant using the Balbach method is simple in construction and operation. Fig. 23 shows the cross-section of a tank. The cathode is made of one-half inch Acheson graphite slabs fitted to the bottom. Two silver contact-pieces rest respectively on the bullion to be parted and the graphite slabs. Bullion cast in thin square slabs is contained in a cloth

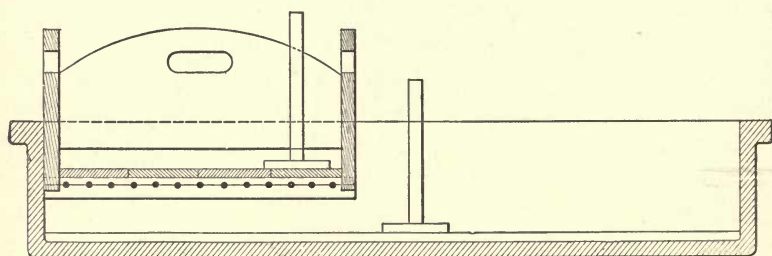


FIG. 23.

case which is supported on a wooden frame suspended over the tank. The gold slimes accumulate on the under side of the bullion, between it and the cathode, increasing the resistance as the operation continues. Each tank has a cathode surface of 8 square feet and a current density of 20 to 25 amperes per square foot used.\* The voltage averages 3.8 per tank, and an average ampere efficiency of 93% was obtained on a continued run, while occasionally an efficiency of 98% was secured. The power required is 31.5 watt-hours per ounce of fine silver produced.

"Most of the silver is deposited on the cathode surface directly under the anode, and the reduction of the distance

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\* The U. S. Metals Refining Co. uses 50 amperes per square foot, 250 amperes per cell. *Engineering and Mining Journal*, May 25, 1907, page 1004.

between anode and cathode is limited by the space necessary to reach in and remove it, which has to be done frequently on account of the silver bridging across to the cathode. This serves also to agitate the electrolyte. There is gassing in this tank and the consumption of nitric acid is much higher than in the Moebius method.

“At 20 amperes per square foot about 32% of the daily output of each tank is held permanently in stock in electrolyte

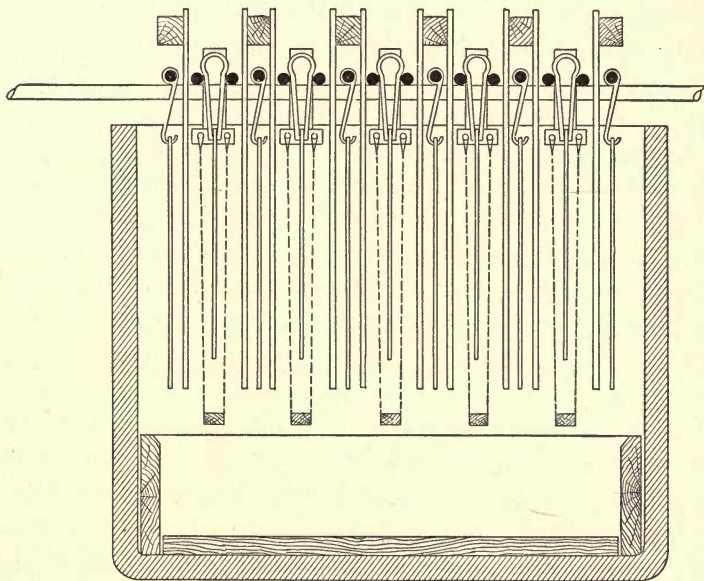


FIG. 24.

and contacts, which is less than is retained in the Moebius method.

“In Fig. 24 is shown the cross-section of a Moebius tank. They are arranged in units of six placed end to end, each unit being provided with apparatus for raising the boxes containing the deposited silver together with the anodes and cathodes, and with arrangements for imparting a reciprocating motion to the wooden scrapers. There is no system of

circulating the electrolyte, but the scrapers moving back and forth agitate it. The anodes are contained in a cloth frame which holds the gold slimes, and the silver is brushed off from the silver cathodes by the wooden scrapers, and drops into a box with hinged bottom. It is removed by raising the boxes above the top of the tanks and emptying it into a tray placed beneath. This operation requires one-half hour per day per unit. Each tank has a cathode surface of about 16.5 square feet, and a current density of 20 to 25 amperes per square foot is used. The voltage between electrodes is 1.4 to 1.5 and the power cost is 13.2 watt-hours per ounce of silver deposited. An average ampere efficiency of 94% is obtained. At 20 amperes per square foot 41% of the daily output of each unit is permanently in stock in cathodes and electrolyte.

"The necessity of cutting out of service the units of a plant using the Moebius method to remove the silver, and the frequent siphoning off and replacing of portions of the electrolyte in each tank, in both the Balbach and Moebius methods, to maintain it of fixed compositions, are objections overcome by depositing the silver on the cathode in an adherent form.

"This method permits of an arrangement of tanks and electrodes and a system of circulation of electrolyte similar to that used in the multiple system of copper refining.

"The finely divided condition of the gold in the bullion, which in commercial work rarely contains more than 40 parts per thousand, requires the anodes to be inclosed in a cloth frame to keep the deposited silver free from gold, as the light, fine particles do not fall to the bottom of the tank with sufficient rapidity. A current density of 10 amperes per square foot is used, and the power cost is nearly identical with the Moebius method. Twenty-eight to 32% of the daily output is retained in cathodes and electrolyte."

The last paragraphs refer to the refining of silver with the nitrate electrolyte, with the addition of gelatine to the solution, for the production of a solid cathode deposit. Mr.



Easterbrooks exhibited some quite solid and very brittle cathode silver, with a nearly smooth surface.

In the Philadelphia mint,\* doré bullion containing 30% of gold is now refined electrolytically with a solution containing 3% of silver nitrate and  $1\frac{1}{2}\%$  of nitric acid, to which a little gelatine is added. Each cell is 40 ins. by 20 ins. and 11 ins. deep, in which are hung 42 anodes  $7\frac{1}{2}$  ins. long,  $2\frac{1}{2}$  ins. wide, and  $\frac{3}{8}$  ins. thick, and 40 cathodes of the same width and length, rolled to 0.016 inch thickness. A current density of 7 amperes per square foot is used. From the above figures it is apparent that an electrode separation of 3 inches or more must be used, which is more than would be necessary if the silver actually comes down solid. The photograph showed the character of the deposit, which probably consists of a large number of roundish masses of silver lightly fastened together, but with sufficient tenacity to keep from dropping into the cells to any serious extent.

The Moebius and Nebel process, using a traveling silver belt to collect the silver, is variously described.† The article by Mr. M. W. Iles ‡ in "The Mineral Industry" gives a rather full description of the plant with observations on the amount of nitric acid used; construction of the gold room; inventory of gold and silver; action of nitric acid on the silver belts; testing of the solution; silver *vs.* platinum contact-points for the anodes, and costs, as follows:

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\* Annual Report of the Director of the U. S. Mint, 1905, abstracted in "Electrochemical and Metallurgical Industry," 1906. Vol. IV, page 306.

† English patent 469 of 1895, January 8th. U. S. A. patents 532209 January 8, 1895; 592097, October 26, 1897; "Electroplating and Electro-refining," Watt and Philip, page 576; Borchers's "Electric Smelting and Refining," 2d Eng. Ed., page 323.

‡ "The Mineral Industry," page 337. Vol. VIII.

TABLE 62.

Supplies.	Per Month.
Oil. . . . .	\$56.20
Nitric acid, 1698 lbs. at 7.5 cents. . . . .	127.35
Waste, 113 lbs. at 9.5 cents. . . . .	10.73
Coal, 25.47 tons at \$2.25 . . . . .	57.31
Coke, 1543 lbs. at \$9.50. . . . .	7.32
Cupels for melting silver. . . . .	6.75
Crucibles, 2 No. 40 at \$2. . . . .	4.00
Sundry supplies. . . . .	21.12
	<hr/> \$290.78
Labor.	Per Month.
Assistant superintendent. . . . .	\$160.00
Five men 31 days. . . . .	379.75
Superintendent half time. . . . .	200.00
	<hr/> \$739.75
Interest \$200,000 at 10%. . . . .	\$1,666.67

TABLE 63.

Cost per Ounce of Bullion.	
Supplies . . . . .	.0427 cents.
Labor. . . . .	.1087 "
Interest. . . . .	.2450 "
	<hr/>
Total. . . . .	.3964 cents.
Royalty. . . . .	.1000 "
	<hr/>
	.4964 cents.

The article concludes with a statement that the cost could be considerably reduced. The rate of interest charged was particularly high.

Through the kindness of the Compania Minera, Fundidora y Afinadora, Monterey, Monterey, Mexico, Mr. A. K. Brewer, Superintendent, I am able to give a photograph of their parting plant, Plate 3, and accurate information regarding it as follows:

Capacity of the plant is 1000 kilos=32,150 ounces per twenty-four hours. The doré runs from 985 to 992 parts per thousand in silver and gold, the gold making up from 2 to 60 parts of the total. The 48 tanks take 250 amperes,

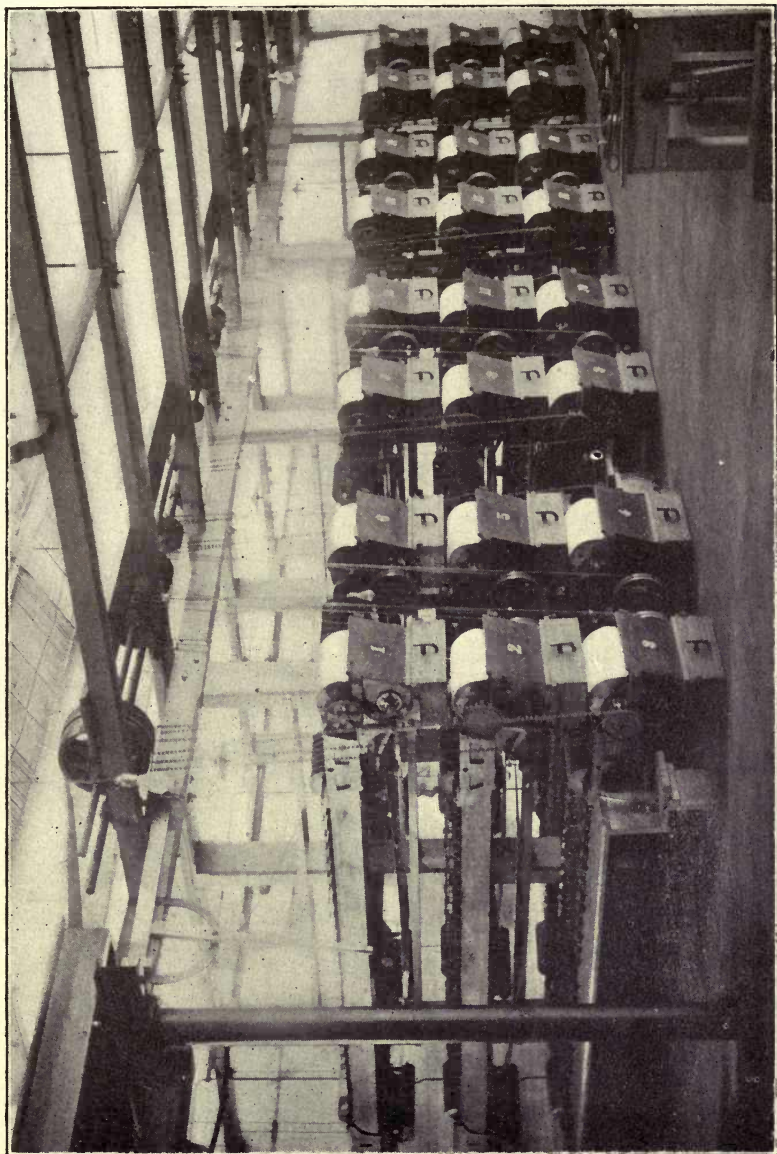


PLATE 3.

SILVER-PARTING PLANT.

Compania Minera. Fundidora y Afinadora, Montercy, Mex.

*page* 161





at 2 volts per tank, equal to 24 K.W. for the whole plant. Five horse-power is used in addition to drive the belts, revolving brushes, and solution pump. The circulation of the electrolyte is perfect and flows from an upper storage-tank through the cells and into a tank under the floor, whence it is raised by the pump to the upper tank. To maintain the solution a few barrels of it are occasionally removed, and added to the ore-beds, so that the values go through the smelter.

The electrolyte contains 20-50 grams silver, 10 to 20 grams copper, 2.5 to 15 grams lead, and 2.5 to 10 grams free nitric acid per litre. Nitric acid is added from time to time to the solution in the lower storage-tank to maintain the electrolyte at working strength.

Each tank takes 22 anodes 3 ins. by 12 ins. by  $\frac{1}{4}$  to  $\frac{1}{2}$  ins. thick, which weigh 0.5 to 2 kilos apiece, so that the amount of silver in the tanks is probably about  $\frac{1}{2}$  to 1 day's output. There is no anode scrap, the anodes being totally dissolved, except the gold. The consumption of nitric acid is about 40 lbs. for 32,000 ounces doré. Men required are three day-times and two at night, including foreman and melter.

It is possible to form a close estimate of the cost of parting with this apparatus, on the above results.

TABLE 64.

	Per Oz.
Power at \$60 per E.H.P. year would be *.....	.0190 cents.
Labor at \$3 average *.....	.0470 "
Nitric acid at 5 cents per lb.....	.0060 "
Interest on doré in tanks at 85 cents per oz.....	.0142 "
Interest on other gold and silver.....	.0284 "
Interest on plant, including solution.....	.0090 "
Fuel and materials for melting.....	.0100 "
Superintendence.....	.0120 "
	<hr/>
	.1456 cents.

\* Assumed.

The costs can not be directly compared with those given below for other methods because of larger scale of operations. Refining 20,000 ozs. per day, the superintendence and labor items would be quite a little higher per ounce, say .019 cents for superintendence, and .063 for labor. Allowing for cost of new belts occasionally, the total cost on a scale of 20,000 ounces per day would approximate to .16 to .17 cents per ounce.

The following description and drawing (Fig. 25) of the Mochius and Nebel apparatus are taken from their U. S. patent:

Referring now to Fig. 25, the letter *A* designates the elec-

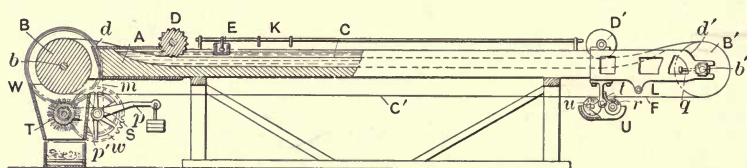


FIG. 25.

trolytic tank, made by preference of a solid block of wood dug out and suitably lined.

*BB'* are rolls adjustably mounted in brackets placed on the tank; *CC'*, an endless silver cathode-belt passing over the rolls *BB'*.

*bb'* are the shafts of the rolls *BB'*, mounted in brackets *dd'* and adjusted by screw-bolts *gg'*, so as to impart to the belt the proper tension.

*DD'* are rolls to keep the part *C* of the belt immersed in the bath, the roll *D* being formed with teeth, as shown, so as not too much to press down the silver precipitated thereon. The roll *D'* may have a plain cylindrical surface.



Slow motion in the direction of the arrows is imparted to the belt  $CC'$  by any suitable means, such as the sprocket-wheels  $Ww$  and chain  $m$ , operated by a belt-pulley mounted on the shaft  $s$  of the small sprocket-wheel  $w$ .

$T$  is a circular brush held against the belt while passing over the roll  $B$  and by a weighted arm  $pp'$ , mounted loosely on the shaft  $s$ , the brush being actuated from the shaft  $s$  by suitable gear, so as to brush the silver from the belt into the receptacle  $R$ .

$U$  is an oil-tank, within which are mounted two rolls  $u$  and  $r$ , both of them a little longer than the width of the belt. As shown, the oil-tank is suspended from the bracket  $d'$  in such a manner that both rolls  $u$  and  $r$  are continuously pressed against the belt. The roll  $u$  is rotated by contact with the lower part  $C'$  of the silver-belt and oils the surface of the same, upon which the silver is afterward deposited when in the position  $C$ . The roll  $r$  is normally held by a pawl  $t$  and serves to remove or scrape off any surplus of oil. By raising the pawl  $t$  the roll  $r$  may be revolved, so as to remove any matter that may have been accumulated thereon. The roll  $r$  is, by preference, made of material such as lampwick properly secured to the shaft in the usual manner. Any other suitable oiling apparatus may be used.

The letter  $E$  designates one of the anode-cells, the anode being connected to the conductor  $K$ , while the belt is connected to the conductor  $L$  by a brush  $F$ .

A great many experiments have been made in my laboratory with the aim of finding a process by which silver could be refined in the same manner that copper and lead are, without the use of any special arrangement to collect cement silver, but to deposit solid silver on the cathodes at once.

•

A number of other objects were in view at the same time. One was to use a solution which would take any bismuth in the anodes into solution. Another was to use a more highly-conducting solution and use higher current density, thus cutting down power and interest.

The best deposits were got with a solution of silver methyl-sulphate. The deposit of silver was adherent and dense, but not entirely solid.

The silver methyl-sulphate electrolyte in distinction from the nitrate electrolyte, can be made strongly acid, and hence highly conducting, a very important advantage in silver refining, as it permits higher current densities. The other electrolytes tried, of silver dithionate and fluoborate, though strongly acid and excellent conductors, would not dissolve bismuth in quantity and gave somewhat inferior results in other respects.

Experiments were also made with amyl-sulphate solutions strongly acid from amyl-sulphuric acid, with and without the addition of gum arabic, etc., and it appeared that there was a point to be reached in respect to strength of solution and percentage of gum arabic, etc., where the deposit was neither bright and loose, nor dark and soft, but smooth and fairly solid.

The deposition of entirely solid silver requires a delicate balance of conditions, and some unexplained phenomena must have presented themselves to experimenters. One curious fact is that a silver electrolyte has to be in use for a considerable number of hours before it gets into good working order and the results at the cathode strongly resemble those obtained in starting up with a new lead solution, when traces of arsenic and antimony come down with the lead and

make it impossible to get a solid deposit. I think it probable that the same thing occurs in the case of silver—that the preparations of silver carbonate, silver nitrate, and silver sulphate, etc., used in making up solutions, contain traces of other elements which deposit with the silver and spoil it mechanically. Possibly a trace of platinum is what does it, or perhaps a modification of silver itself. It is known that sometimes more silver deposits than is demanded by theory, and it has been suggested that this is due to the deposition of colloidal particles of silver. In support of the above ideas, at one time I prepared a solution for depositing silver, by electrolysis of the solution with a silver anode in a diaphragm-cell. The resulting solution was one of silver methyl-sulphate, and gave a beautiful bluish, smooth, solid deposit of silver, not inferior in structure to electrolytic copper.

The use of a higher anode current density, that is, above say 20 or 30 amperes per square foot, is undesirable with the methyl-sulphate solution. On one occasion a methyl-sulphate solution that was yielding a dense deposit of silver gave a very poor deposit soon after the substitution of a smaller and purer anode, the current and cathode area remaining the same.

The use of perchlorate of silver, which has been used by Carhart, Willard, and Henderson\* in the silver coulomb-meter with much better results than were formerly obtained with silver nitrate, is analogous to the use of methyl-sulphuric acid, as it is also a strong acid that can be used in large excess above that required to dissolve the silver.

Methyl-sulphuric acid is prepared by mixing together

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\* Am. Chem. Soc., Vol. IX, page 395.



methyl alcohol and sulphuric acid. The mixture heats up, and the reaction only takes a short time. Previous results that indicated a period of eight to ten hours' reaction at 100° C. and statements in text-books to the same effect are wrong, and it is doubtful if the reaction takes more than time enough for mixing.

I had experiments made in my laboratory with various mixtures of 96% sulphuric acid and 88% methyl-alcohol, with different heat treatment. The best results were got by simply adding the alcohol to the acid, mixing well, allowing it to stand five minutes, and pouring into cold water (pouring on ice would be better in practice).

The results in that way were as follows:

TABLE 65.

No.	H <sub>2</sub> SO <sub>4</sub>	Wood Alcohol.
1	20 cc.=35.8 gr. H <sub>2</sub> SO <sub>4</sub>	15 cc.=10.9 gr. CH <sub>4</sub> O
2	20 cc.=35.8 gr. H <sub>2</sub> SO <sub>4</sub>	12 cc.= 8.8 gr. CH <sub>4</sub> O
3	20 cc.=35.8 gr. H <sub>2</sub> SO <sub>4</sub>	10 cc.= 7.3 gr. CH <sub>4</sub> O
4	20 cc.=35.8 gr. H <sub>2</sub> SO <sub>4</sub>	8 cc.= 5.85 gr. CH <sub>4</sub> O
5	20 cc.=35.8 gr. H <sub>2</sub> SO <sub>4</sub>	6 cc.= 4.4 gr. CH <sub>4</sub> O

No.	H <sub>2</sub> SO <sub>4</sub> Utilized.	Alcohol Utilized.
1	48% of total	51% of total
2	42% " "	56% " "
3	38% " "	61% " "
4	33% " "	66% " "
5	30% " "	80% " "

With C.P. methyl-alcohol, specific gravity .817=92%, the result was as follows:

TABLE 66.

		H <sub>2</sub> SO <sub>4</sub> Utilized.	Alcohol Utilized.
20 cc.=35.8 gr. H <sub>2</sub> SO <sub>4</sub>	12 cc.=8.9 gr. CH <sub>4</sub> O	47% total	61% total
20 cc.=35.8 gr. H <sub>2</sub> SO <sub>4</sub>	10 cc.=7.44 gr. CH <sub>4</sub> O	42% " "	65% " "
20 cc.=35.8 gr. H <sub>2</sub> SO <sub>4</sub>	8 cc.=5.95 gr. CH <sub>4</sub> O	37% " "	72% " "

The formation of water prevents complete reaction. The materials used in the experiments already contained water. With anhydrous materials the results must be better. Better results still are got with fuming  $\text{H}_2\text{SO}_4$ , which is now procurable at about 1.3 cents per lb. for acid containing 30% of  $\text{SO}_3$ . EXPERIMENT: 155 grams fuming  $\text{H}_2\text{SO}_4$  containing 30%  $\text{SO}_3$ , 20 cc. concentrated  $\text{H}_2\text{SO}_4$ , and 75 cc. wood alcohol 88%, added together in small portions, first one and then the other, starting with alcohol and ordinary  $\text{H}_2\text{SO}_4$ , gave a yield of 53% on the acid and 67% on the alcohol. For comparison with the above results, the proportions of  $\text{SO}_3$  and alcohol in this experiment are the same as with 20 cc. 96%  $\text{H}_2\text{SO}_4$  and 13.5 cc. alcohol, when the yield on acid is about 46% and on alcohol, say 54%.

The course of the reaction was traced by titrating a sample with ammonia and cochineal. Acid disappears in the reaction, as one molecule of dibasic acid produces one molecule of a monobasic acid, and the amount shown by titration to have disappeared multiplied by two gives the amount of acid utilized, from which can be calculated the amount of alcohol combined.

In practice the product is poured on ice and the liquid treated with lead carbonate (though lime or baryta would also do) in amount sufficient to remove all  $\text{H}_2\text{SO}_4$ . The filtrate from the lead or calcium or barium sulphate is then treated with silver carbonate (from silver sulphate and soda) when the solution is ready for use if of the right strength, namely, about 15%  $\text{CH}_3\text{SO}_4'$  and 4-6% Ag.

Probably ethyl alcohol can be used equally as well, but considering the relative molecular weights ethyl alcohol would have to be 1.425 times as cheap as wood alcohol, to compete.

A current density of 20 to 30 amperes per square foot is

permissible, and the solution, with agitation, may be reduced to 1.5 grams of silver per 100 cc. before it is necessary to strengthen it up again. The addition of gelatine or other materials is not recommended at present, as they are hard to control in their action and the deposit is as satisfactory without. The anodes should be wrapped in cloth. Silver-plated and slightly greased graphite cathodes may be used to advantage, to which the silver adheres though not very securely. After one day's refining the cathodes are removed and the silver split off and the cathodes returned to the bath. As some silver is likely to be knocked off in the cells, the use of storage-battery glass cells is convenient. These can be handled and cleaned easily, and will take a fairly large current. A cell about 12" square and 15" deep can easily take 110 amperes, and perhaps as high as 200, while a stoneware Balbach cell about 4 feet long, 1 foot deep, and 2 feet wide, is only good for about 100, perhaps 200 amperes, and takes up eight times the space.

The cost of refining by the various electrolytic methods can be estimated as follows, from various data. In all cases the interest on the original cost of plant is taken at 10% and on metal on hand at 6%. It is evident that the cost of melting doré bullion and refined silver will be practically the same in all cases.

Comparative cost, refining 20,000 ozs. per day, Table 67.

TABLE 67

	Cents per Oz.		
	Moebius.	Balbach.	Betts.
Interest on plant, including solution. ....	.0090	.0088	.0042
Power at \$60 per E.H.P. year. ....	.0146	.0369	.0049
Interest on doré, in cells at \$0.85 oz. ....	.0142	.0142	.0142
Interest on other gold and silver in stock. ....	.0284	.0284	.0284
Labor and superintendence. ....	.0850	.0850	.0850
Chemicals. ....	.0100	.0150	.0100
Fuel and material for melting. ....	.0100	.0100	.0065
	<hr/>	<hr/>	<hr/>
	.1712	.1983	.1532



The above figures can be expected to be fairly close, but the fact that the Balbach method, as modified by Mr. Wm. Thum,\* has been recently introduced in new plants, speaks against the above figures. It is difficult to see wherein the new process has the advantage over the Moebius, unless in the matter of labor cost or possibly interest on doré in the cells. It seems, however, probable that the above figures for the Balbach process are a little too high. One manager remarked to me that he thought the cost of operating the Moebius and Balbach process about the same, with the advantage of simplicity in favor of the latter.

When it comes, however, to refining doré bullion containing important quantities of base metal, as copper, lead, or bismuth, the results are somewhat different, and can be best expressed by a formula of the form

$$C = A + xC + yB + zP,$$

in which  $A$  is the cost of melting and refining an ounce of doré free from base metals, and  $C$ ,  $B$ , and  $P$  are the costs of recovering from the electrolyte, as marketable metal, one ounce each of copper, bismuth, and lead respectively, and adding the equivalent of silver to the solution, while  $x$ ,  $y$ , and  $z$  are the respective proportions present.

In the Moebius and Balbach processes the cost of recovering bismuth per Troy ounce from the anode slime would approximate as follows:

For washing gold with soda to form the soluble variety of bismuth hydrate or carbonate, and dissolving in cold nitric acid

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\*U. S. Patent.

heating the solution to precipitate basic nitrate, about 0.13 cent.....	0.13 cent.
Converting basic nitrate to metal by smelting with charcoal, about 0.13 cent.....	0.05 "
Silver carbonate to make up for weakening of electrolyte.....	0.48 "
<hr/> Ttotal.....	<hr/> 0.64 cent.

For copper, copper nitrate can be crystallized out and this could be electrolyzed in a dilute solution for copper and nitric acid, and the nitric acid returned to the bath, though this is not probably actually done.

Estimated cost per Troy ounce copper in bullion..... .3 cent.

If lead nitrate crystallizes with the copper nitrate, evidently the two may be dissolved together and the copper deposited out with platinum or carbon anode as above, while the residual lead nitrate can be crystallized from the mother liquor, lead peroxide being also produced, however.

Estimated cost of evaporating lead nitrate per Troy ounce and corresponding loss of nitric acid..... .3 cent.

If the doré should contain then 10% lead, 10% bismuth, and 10% copper, the cost per ounce ought to approximate to the result given by the formula above.

$$C = .18 + \frac{1}{10} \cdot 64 + \frac{1}{10} \cdot 3 + \frac{1}{10} \cdot 3 = .304 \text{ cent.}$$

With the Betts parting process the values would be somewhat different, and considerably lower, for (1) there is no appreciable loss of the acid making the basis of the electrolyte, (2) no separate operation for removing bismuth from the gold slime, and (3) the working up of the copper-silver pre-



precipitate thrown out by metallic bismuth and the bismuth and copper thrown out by metallic lead, by treatment with ferric sulphate, hot sulphuric acid, etc., is simpler and direct. I should estimate the values for *C*, *B*, and *P* at .5 cent, .2 cent, and .1 cent, respectively. If these values are realized, the cost for the same doré bullion would be

$$\text{Cost} = .17 + \frac{1}{10} \cdot .5 + \frac{1}{10} \cdot .2 + \frac{1}{10} \cdot .1 = .215 \text{ cent.}$$

These results are not intended to be entirely accurate, and of course they can not be.





## CHAPTER V.

### THE MANUFACTURE OF HYDROFLUORIC AND FLUOSILICIC ACIDS.

\* "No very useful literature on this subject exists to the best of my knowledge. Most chemists regard it as an extremely dangerous substance, and have presumably left it alone as much as possible. Yet hydrofluoric acid and fluorides have an extending use for numerous purposes. Its preparation is easy and safe, if proper precautions are taken.

"Samples of fluorspar may be tested by mixing say 50 grams with various proportions of 66° sulphuric acid in small sheet-iron pans and distilling under the hood. For preparation in small quantities for the laboratory, apparatus as shown in Fig. 26 gives good results if used out of doors. The retort is an ordinary cast-iron pot, perhaps one foot in diameter and 6 inches deep. The cover is made by filling with sand to near the top, leveling it off and pouring in about  $\frac{1}{2}$  inch of lead. The lead pipe is separate from the cover, and passes over to a lead hydrofluoric-acid bottle containing water. The water must not come as high as the end of the lead pipe.

"During distillation the bottle is sprayed with water from a hose to keep it cool. A charge of about 2 kg. of fluorspar and 2.5 kg.  $\text{H}_2\text{SO}_4$  66°, is stirred up in the pot. The

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\* By permission of the *Engineering and Mining Journal*, April 20, 1907.

fluorspar, for the most part, dissolves immediately on stirring in the sulphuric acid, without evolution of much fume, until heat is applied. The cover is put on and dry cement put over the joints as a lute, cement being suitable for this purpose.

"The heating should be moderate at first to prevent too much frothing in the pot. Distillation takes two or three

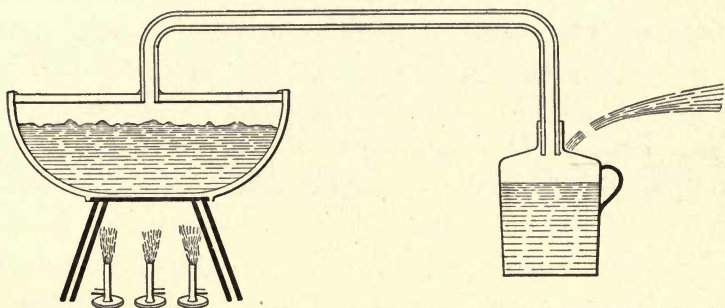


FIG. 26.

hours, and the end can be told by feeling of the lead pipe near the bottle, which is hot as long as acid is coming over. Very little loss is experienced and a yield of 80% or thereabout, is obtained.

**"Operation on larger scale.**—On a large scale, the application of the same principles is successful. The general arrangement is shown in Fig. 27, for which a few explanations are necessary. The pot may be cast about 8 ft. in diameter, 3 ft. deep at the center, and 1 in. thick, with a slightly curving bottom to prevent cracking. For the pot a cast-iron cover 1 in. thick is used, dipping into the annular trough around the pot, which contains strong sulphuric acid as a seal. All the other seals are made in the same way, but water may be used for the joints on the condensers where the temperature

is not so high. Lead retorts and lead covers for the retorts are useless.

"The condensers consist of a series of two or three lead boxes of about 1 cu.m. capacity, entirely submerged in a water-tank and partially filled with water or dilute HF. Condensers should be made of heavy lead, supported by wooden pieces to which the lead is attached by means of lead straps burned on. The lead delivery-pipes may be about 5 in. in diameter. The condensers have an overflow so that the acid

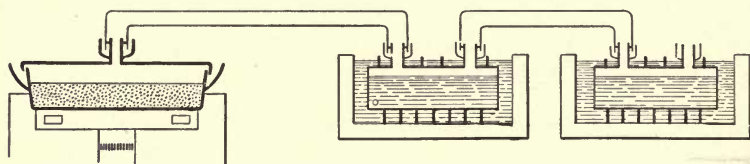


FIG. 27.

never can rise to the end of the delivery-pipe. If this happened, a partial vacuum might result, and draw water back into the pot, where it would probably cause an explosion.

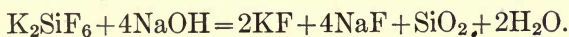
"The charge may consist of 1000 lbs. of ground fluorspar and 1000 to 1200 lbs. 66° sulphuric acid.  $\text{SiF}_4$  comes off first and deposits silica on the water in the first condenser, stopping absorption somewhat, so that it is necessary to stir the water in the first condenser until most of the  $\text{SiF}_4$  has come over. The pot may be charged in the morning and distillation finished by night. Coal is used for fuel, burned on a grate of about 3 square feet. The residue in the pot is comparatively hard, and, after cooling, is dug out with pick and shovel. The yield of acid calculated on the sulphuric acid used is approximately 80 to 90%.

"The cost of manufacture is not great, the principal items being the raw materials necessary. To produce 1 lb.



anhydrous HF, about  $2\frac{1}{2}$  lbs. of fluorspar and 3 lbs. sulphuric acid are necessary. Fluorspar and sulphuric acid are worth about \$10 to \$15 a ton, making a cost for raw materials, exclusive of coal, of approximately  $2\frac{3}{4}$  to  $4\frac{1}{8}$  cents per pound anhydrous HF.

**“Method of analysis.**—The sample of acid is mixed with several times its bulk of nearly saturated and neutral potassium nitrate solution. This causes a precipitation of potassium fluosilicate in the solution: Phenolphthalein is used as indicator, and the solution titrated with caustic soda in the cold. This gives the total of the HF and  $\text{H}_2\text{SiF}_6$  present. The sample is then heated to boiling, when it will be found that considerable more caustic soda may be run in to get another end point. In the first titration, the HF present and the  $\text{HNO}_3$  liberated by the reaction of potassium nitrate and fluosilicic acid are neutralized by the alkali. When titrated hot, the precipitated  $\text{K}_2\text{SiF}_6$  is decomposed by the alkali. The following is the equation involved:



“The rule for calculating is, 1 gr. NaOH used in the second titration = 0.9 gr.  $\text{H}_2\text{SiF}_6$  in the sample. For HF present divide the number of cubic centimeters of NaOH used in the second titration by 2, and subtract the result from cubic centimeters used in the first titration. The remainder shows the HF, 1 gr. of NaOH equalling 0.5 gr. HF.

“Hydrofluoric acid has been shipped in beer-barrels with rosin lining, which are entirely successful, and last for some time and for long shipments; also in rectangular lead carboys. Its storage in lead is not very satisfactory on account of the

corrosion of the lead. Probably the presence of sulphuric and fluosilicic acids has some effect in the corrosion.

"I am indebted to Dr. William Valentine for some of my data."

The conversion of hydrofluoric acid to fluosilicic acid can be accomplished in a lead-lined tank as shown in Fig. 28.

The tank may be made about 5 or 6 feet square and is one-third filled with clean sand or broken quartz. The method of operation is based on the discovery that while cold hydro-

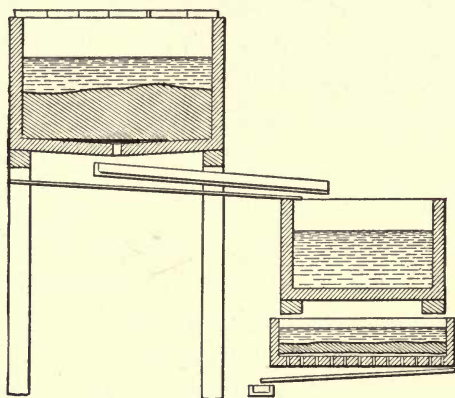


FIG. 28.

fluoric acid will pass through sand and be only partly converted to  $\text{H}_2\text{SiF}_6$ , if the acid is hot, the reaction will easily maintain the heat and pure  $\text{H}_2\text{SiF}_6$  will run through. Accordingly on the start the tank is filled with water and steam blown in to heat it to boiling. When the water running through begins to get hot, it is allowed to drain off, and 30-35% acid added. The tank is kept covered by boards, but acid would boil off in large quantities, except for the addition of cold water in sufficient amount to prevent this. As the acid runs out of the tank (one square foot of sand at Trail used to let

acid through at about the rate of one barrel in twenty-four hours) more is added, with enough cold water to prevent boiling off of acid. As long as the supply of acid is maintained the tank will not cool off, and the acid running through has only to be diluted and have white lead added.

The tank should be elevated so that the products can run off into other tanks. At Trail the acid was hoisted to the tank in barrels, the bung knocked in, and the acid poured into the tank. This was a very disagreeable job. A lead-lined montejus, if a supply of acid under pressure is available, would be much better to work with. When convenient the hydrofluoric acid is made on the hillside above the works, so that it may be entirely managed by gravity.



## CHAPTER VI.

### CHOICE OF CONSTANTS.

THIS chapter will be a study of the relative advantages of various rates of working, arrangement of plant, methods of slime treatment, etc.

Probably the chief point to be decided is the current density to be used in depositing the lead. The problem can be looked at on many sides, but most of these can be eliminated at once as having no real influence on the result.

There is the choice to be made between the series and multiple arrangements of electrodes. The important advantages of the two are probably as follows:

**Series system.**—Power cost about 40%–50% less, or a saving of about 34 K.W. hours, worth about 28 cents per ton.

No starting sheets required, or a saving of about 15–20 cents per ton over lead cathodes, and much less over lead-plated steel cathodes.

Smaller construction cost for plant, excluding power plant, of about \$50 per ton per day, or at 10% per annum for interest, 4 cents per ton.

Total of advantages, about 50 cents per ton.

To offset this, the multiple process will require only about half as many anodes cast and charged, and will produce less anode scrap, an advantage of 10–15 cents probably.

No necessity of separating anode scrap and slime from cathode lead, an advantage that might easily be 20 cents per ton and probably more, while producing better refined lead, too. Less interest charge on anodes, which might easily be about 5 cents per ton. Total of advantages, 35-40 cents per ton, or more.

There are probably other disadvantages connected with the series system that are only familiar to those who have had experience with it.

The character of the bullion would have to be carefully considered in this connection. The series process would succeed best with lead bullion giving very little slime, such as Missouri lead or relatively impure bullion containing  $1\frac{1}{2}\%$  of antimony and arsenic or more. With this latter kind of lead the slime remains closely adherent, and probably the entire anode could be dissolved through and the process stopped when the cathode lead on the other side was being first attacked. The slime would remain as a soft, porous slab separate from the cathode lead. With the average grades of bullion containing little arsenic and 0.5-1% antimony, the slime is so voluminous and soft that it would be apt to slip off the anode and fill most of the space between the electrodes, which condition could perhaps be remedied by making the tanks nearly twice as deep as the electrodes, with boards placed across the tank every foot or so to prevent the current passing through the bottom part to a large extent.

The published information on the series process as applied to copper is not entirely applicable to lead. One of the great objections to the series system in copper refining is the cost of making smooth and uniform electrodes. This would be much easier with lead, on account of the greater facility of

melting and rolling it. The separation of anode scrap from deposited metal, said to cost 60 cents per ton with copper, would not be nearly so large an item with lead.

With little probability of doing much better with the series system, and some of doing worse, there is little chance of its being attempted, except for small plants in which it is never convenient to generate large currents of high amperage and low voltage, or where power is very expensive.

Even for small plants another system proposed,\* which combines to some extent the advantages of the two systems,

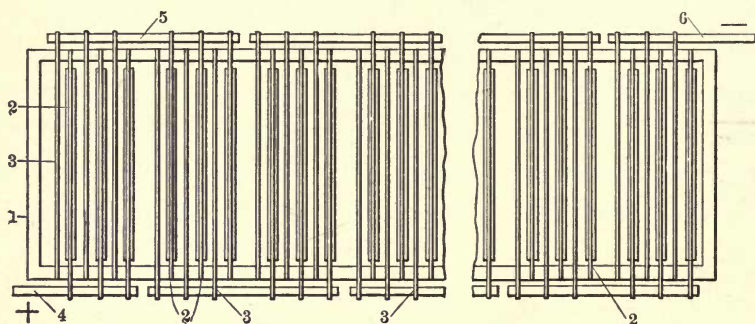


FIG. 28a.

is apt to be better than the series system. The principle of this arrangement can be easily noted from Fig. 28a.

With certain improvements in the multiple process that seems feasible, and are noted elsewhere, the multiple process would have a decided advantage over the series process.

We have these points to consider in choosing current density:

(1) *Purity of the lead.*—Obviously the current could be so high as to dissolve impurities which would deposit on the

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\* U. S. Patent 789353. May 9, 1905.



cathodes. This is not a factor having any important influence in choosing the current density, as it has been amply demonstrated that pure lead can be produced over any range of current density that is permissible from other considerations.

(2) *Cost of glue used in the solution.*—It seems probable that the consumption of glue increases with increase of current to some extent. As the amount of glue used per ton of lead produced is only about one-half to three-quarters of a pound, it will be seen that a small increase or decrease of this amount is too small a factor to be considered.

(3) *Low current density* means larger tank room and consequently somewhat greater cost of building. Each ampere per square foot below 12 amperes, would make an extra cost of building of approximately \$20 per ton refined per day, while increasing the current up to say 20 amperes would save approximately \$100 per ton per day on this score. Capitalized at 10%, the total difference between 10 and 20 amperes is only about 3 cents per ton. In some circumstances the value of land will enter into the question, but in that event it may be better to economize in space by leaving smaller passages between the tanks, and making the tanks somewhat deeper. At the plant of Locke, Blackett & Co., Ltd., Newcastle-on-Tyne, this method was adopted, and the current is 12 amperes per square foot, with a space between the rows of tanks and around the sides of about 20 inches. This is hardly as convenient, but it makes little if any difference in the cost per ton refined.

(4) *Interest on metal tied up.*—We can calculate the thickness of metal dissolved per week at various current densities, at 95% efficiency, as follows, Table 68:

TABLE 68.

Current Density Amperes per Square Foot.	Inches of Anode Dissolved per Week, on Each Side.
10	.243
12.5	.305
15	.365
17.5	.425
20	.486

The amount of metal tied up may be varied by varying the thickness of the anodes, but it is, of course, uneconomical to cast them very thin on account of the extra cost of casting, placing in tanks, cleaning, etc. The best thickness of anode is really dependent mainly on the thickness of the cathodes it is possible to make. Each set of anodes should be made so as to give either one or two sets of cathodes deposited as thick as practicable. Present experience indicates that cathodes with about 35 lbs. deposited per square foot are as heavy as it is desirable to make them. For an anode yielding two sets of cathodes, and allowing 15% for scrap to be remelted and slime, makes a 500-lb. anode with the usual size, 2 feet wide and 3 feet deep. With various current densities, bullion valued at \$175 per ton, an average of five-sixths of the total value being in tanks, and allowing one day's supply unmelted cathodes and one in stock, and half day for melting each, the results are as follows:

TABLE 69.

Current Density.	Ins. Dissolved per Week, Both Sides.	Value of Metal on Hand per Ton Refined per Day.	Int. Charges per Ton Refined at 6%.
10	.486	\$2570	\$0.423
12.5	.608	2160	0.355
15	.73	1885	0.310
17.5	.85	1690	0.278
20	.974	1550	0.255

The interest charge with the low current density is quite considerable, and could be reduced to perhaps two-thirds that amount by casting anodes one-half as thick; but the extra cost of casting and handling so many more pieces would leave little or no net saving.

(5) *Depreciation of tanks.*—With the wooden tanks hitherto used, the life of which may be taken at four years, and costing \$40 each, evidently higher current density means the maintenance of fewer tanks in a direct ratio, about as follows, allowing for a certain amount of repairs:

TABLE 70.

Current Density.	Depreciation of Tanks per Ton Refined.
10	\$0.143
12.5	0.114
15	0.095
17.5	0.081
20	0.071

(6) At Trail the current density is about 16 amperes per square foot, and the total *loss of acid* is stated to be 10 lbs. of anhydrous  $\text{H}_2\text{SiF}_6$  per ton,\* the solution containing 6–7 gr. lead and 12–13 gr.  $\text{SiF}_6$  per 100 cc. At Newcastle-on-Tyne current density 11 amperes, the loss at one time was determined as 6 lbs. per ton of 2240 lbs., the solution containing 6 gr. lead and 15 gr.  $\text{SiF}_6$  per 100 cc.

The acid loss at Trail in 1902 and 1903 was as follows:

TABLE 71.

August and September 16, 1902	13.8 lbs. $\text{SiF}_6$ per ton lead.
September 16–October 6, 1902	7.7 " $\text{SiF}_6$ " " "
January 22–February 13, 1903	6.3 " $\text{SiF}_6$ " " "

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\* Communicated by Mr. A. J. McNab, Trail, B. C. See Appendix.



In the last two determinations the current density was about 12 and 10 amperes per square foot respectively, with solutions containing 7.5 gr. and 8.5 gr.  $\text{SiF}_6$  per 100 cc. respectively. These figures are still too high for good work, as the arrangements for saving leaks and wash-waters were crude. This should be noted especially for the first period, as operations had not been at all systematized then.

The use of a high current density would tend to diminish acid loss from leaks, but there need be no loss from leaks anyway with good tanks and proper supports. The only way in which high current density could increase acid loss would be by depositing silica in the slime faster than the free HF in solution could dissolve it, but that means only a loss of the relatively valueless silica, which can be cured by dissolving fresh silica in the solution, or by stirring the slime up well with the electrolyte to secure a recombination of silica and HF. The latter simple and practicable procedure has not yet been introduced in practice, as far as I know.

Lacking determinations of acid loss at varying current densities, and in view of the facts we have which do not make it seem probable that moderately higher current densities would increase the acid loss, it would not be safe to speculate much on the effect of varying current density.

(7) *Interest on copper conductors.*—This is not a variable in respect to current density to any extent, and need not be considered in the present inquiry.

(8) *Interest on tanks and electrolyte* is a small item of a few cents only and not worth considering in this connection. The difference in the solidity of the lead and labor cost for keeping tanks in good working order is not considered to

vary appreciably with variation in current density, within the limits considered here.

(9) *Power*.—The power cost per ton varies in nearly direct proportion to the current density, and also of course with the cost of electrical power, and this latter may be taken at \$50 per E.H.P. year, which seems a high enough average. It is now possible, by the use of gas-engines, water-power, or cheap coal, to generally reach or surpass this figure. It is also possible to secure wide variation in power cost, by varying the strength of the electrolyte. Inasmuch as even with a low current density of say 10 amperes per square foot, it is economy to use a rather strong solution containing about 16 gr.  $\text{SiF}_6$ '' per 100 cc. (except where acid is unduly expensive), my figures are based on a solution of 7–8 gr.  $\text{Pb}$ '' and 16–17 gr.  $\text{SiF}_6$ '' for various current densities, and also for comparison, with a solution containing 10 gr. lead and 20 gr.  $\text{SiF}_6$ . For conductivity determinations, see Tables 18 and 19 and Figs. 2, 3, and 4.

The temperature effect, although the conductivity varies quite a little with change of temperature, is not of much practical importance. At Trail at one time the electrolyte was heated as high as  $50^\circ$ , by a steam coil in the circulation-tank, but the practice was found unsatisfactory in several ways, while the gain in conductivity was not large.

The effect of temperature up to  $30^\circ \text{C}$ . is illustrated in Figs. 3 and 4. The resistance was not measured at higher temperatures, but can be safely calculated to about  $45^\circ$  by extrapolation. But as, up to the present, heating the solution beyond  $30^\circ \text{C}$ . has not been a success, this temperature will be assumed for the purpose of calculation. The effect of the current itself is found to maintain the solution at this tem-

perature the year round, the buildings being heated in winter. Electrode separation is taken as  $1\frac{3}{4}$  inches, which is permissible in practice. The figures in Table 72, are not intended to give the total power cost, but only that part of it which varies with variation in current density. The other losses of power, as copper losses and contact losses, should be taken as constant for all current densities, for these losses do not depend on current density, but on other independent matters, as cost of copper for bus bars, and cost of labor cleaning contacts, the economical balance for these items being about the same regardless of current density. Power is taken at \$50 per E.H.P. year.

TABLE 72.

Current Density Amperes per Square Foot.	Volts from Re- sistance of Solution.	Polarization Volts.	Total Volts.	Power Cost at 95% Efficiency.
10	.164	.02	.184	\$0.352
12.5	.205	.02	.225	0.430
15	.246	.02	.266	0.504
17.5	.288	.02	.308	0.590
20	.328	.02	.348	0.665

The actual total power cost for depositing is about \$0.18 higher on account of losses in conductors and contacts.

From Fig. 24, taking the 30° C. curve, the use of a solution containing 10 gr. lead and 20 gr.  $\text{SiF}_6$  per 100 cc. would reduce the resistance from 1.35 ohms per inch unit in the above case to about 1.05 ohms, when the power cost would be somewhat less, particularly for the higher current densities, as follows:



TABLE 73.

Current Density Amperes per Square Foot.	Volts from Re- sistance of Solution.	Polarization Volts.	Total Volts.	Power Cost 95% Efficiency.
10	0.128	0.02	0.148	\$0.280
12.5	0.159	0.02	0.179	0.350
15	0.191	0.02	0.211	0.392
17.5	0.224	0.02	0.244	0.453
20	0.255	0.02	0.275	0.511

Even stronger solutions than this I have used in 500-lb. runs, but the strongest solution yet used in practice contains about 17 gr.  $\text{SiF}_6$  per 100 cc.

Our final comparison will take into account power cost, depreciation of tanks and interest on metal, the other elements entering into the question being small as far as is known, and may be assumed to neutralize each other:

TABLE 74.

Current Density.	Tank De- preciation.	Interest on Building, Difference.	Interest on Metal.	Power Cost.		Total.	
				A	B	A	B
10	\$0.143	\$0.030	\$0.423	\$0.352	\$0.289	\$0.948	\$0.885
12.5	0.114	0.023	0.355	0.430	0.350	0.922	0.842
15	0.095	0.015	0.310	0.504	0.392	0.924	0.812
17.5	0.081	0.008	0.278	0.590	0.453	0.957	0.820
20	0.071	0.000	0.255	0.665	0.511	0.991	0.837

While there is not much to choose, the cheapest current density is about 15 amperes per square foot. In view, though, of the slight differences in operating cost, the choice of current density will then be largely influenced by other factors, as first cost of plant and elasticity of tonnage treated with the plant.

From the standpoint of first cost of plant, on one hand we can increase the tank capacity and cut down the size of the power plant, and on the other, by increasing the power plant we can cut down the cost of the tank plant. I will assume that, per ton refined per hour, the power plant must furnish 23.6 K.W. to overcome contact and other metallic resistance anyway ( $=.1$  volt per tank average), and a variable amount of power depending on the current density as follows:

TABLE 75.

10	45.2 K.W.	68.8 total K.W.
12.5	55.2 "	78.8 " "
15	65.4 "	90.0 " "
17.5	75.8 "	99.4 " "
20	85.8 "	109.4 " "

The cost of power plant may be roughly taken as \$135 per K.W., and of the tank plant, disregarding handling machinery and copper bus bars as practically constants, but including tanks, electrolyte, and floor area, at \$15,000 per ton per hour, with a current density of 12.5 amperes.

Cost of variable items in plant for solution with 17 gr.  $\text{SiF}_6$  per 100 cc.:

TABLE 76.

Current Density.	Power Plant.	Tank Plant.	Total.
10	\$ 9,270	\$18,750	\$28,020
12.5	10,650	15,000	25,650
15	12,150	12,000	24,150
17.5	13,400	10,714	24,114
20	14,750	9,375	24,125

With the stronger solution, 20 gr.  $\text{SiF}_6$  and 10 gr. Pb per 100 cc.

TABLE 77.

Current Density.	Power Plant.	Tank Plant.	Total.
10	\$7,960	\$20,000	\$27,960
12.5	9,050	16,000	25,050
15	9,370	13,333	22,703
17.5	10,350	11,428	21,778
20	11,250	10,000	21,250

From these results it appears that in future progress will tend to higher current densities and stronger solutions, and will reach probably 20 amperes per square foot, if no unforeseen objection crops up.

A plant built for 15 amperes per square foot can be arranged as to be able to stand a 33% overload if the solution is strengthened up somewhat.

No combination of current density and solution strength should be used, at which a solid lead deposit may not be obtained, otherwise the increased acid loss would offset any advantage gained.

**Choice of slime process.**—Out of a large number of slime processes described in more or less detail in Chapter II, the following only will be considered as being available at the present time for practical work, the others being too little developed or to apply only to special cases. The sodium sulphide process has been given an extensive trial at Trail, but full particulars have not yet been given out. The processes considered below have been the subject of much experiment and have been or will probably be used in practical work.

(1a) Melting with sulphur to matte and slag, especially for slime containing little or no bismuth.



(1b) Melting to doré, matte, and slag, especially for slime containing bismuth.

(2) Extraction of copper and arsenic in sulphuric acid solution and antimony from the residue with hydrofluoric acid. Oxidation to be secured by (c) roasting with sulphuric acid, (d) drying in air, and (e) by ferric sulphate produced electrolytically.

Process (1a) converts the copper and silver present into cuprous and silver sulphides, which have to be reduced to metal and electrolytically refined. All methods of converting the matte into metal so far successful are fairly expensive, and for that reason this process shows up at a disadvantage compared with the others, when the amount of silver and copper are at all large. But for slime containing only a little copper and silver this process will do excellently. Assuming that the lead bullion being refined contains 50 ozs. silver per ton and 0.2% copper, beside 20 lbs. of antimony and 8 lbs. of arsenic, the costs would be about as follows, on a large scale of say 100 tons of lead per day:

TABLE 78.

	Per Ton Lead.
Drying and oxidizing slime (Fig. 57).....	\$0.05
Melting in iron pot, coal, labor, repairs (Fig. 58).....	0.08
Sulphur, 2 lbs. ....	0.03
Grinding matte, heating with $H_2SO_4$ , and melting. Coal, labor, repairs, $H_2SO_4$ . ....	0.11
Electrolytically refining alloy for copper. ....	0.04
Melting and refining silver. ....	0.11
Grinding and leaching slag for $SbF_3$ solution, and smelting and refining $PbSO_4$ residue.....	0.12
Depositing 20 lbs. antimony.....	0.40
	<hr/> \$0.94

Process (1*b*). For lead bullion containing 20 lbs. antimony, 2 lbs. copper, 6 lbs. arsenic, 2 lbs. bismuth, and 70 ozs. silver per ton, the costs are calculated to be about as follows:

TABLE 79.

	Per Ton Lead.
Drying and oxidizing slime . . . . .	\$0.05
Melting in iron pot. . . . .	0.08
Treating matte as above. . . . .	0.05
Electrolytically refining doré, and recovering bismuth, copper, silver, and gold. . . . .	0.21
Grinding and leaching slag as above. . . . .	0.12
Depositing 20 lbs. of antimony. . . . .	0.40
	<hr/> \$0.91

Usually slime will contain too much copper for the above processes, and this would be more certain in future for electrolytic refineries, as I will attempt to show. Very often lead bullion as it flows from the lead-furnace contains copper. As the smelter has not been paid anything for copper in his bullion, and can get something, though nowhere near its full value, if in matte, usually the lead bullion is cooled and skimmed in the lead "cooler," the dross with or without liquating as much lead as possible, going back to the blast-furnace, and the copper being eventually recovered as a matte containing probably on the average 40% of copper and 10-15% lead. The lead in this matte is not usually paid for or recovered, and counting in the lead loss, the copper of the dross has been reduced in value by as much as 6 cents per pound. In refining bullion by the Parkes process, the refiner has no advantage over the smelter in recovering copper, as the refinery also puts the dross through a lead-furnace. An electrolytic refinery is, however, free from these objections, and certainly



when the smelter and refinery are under the same control the practice of skimming off as much dross as possible will be found uneconomical. Custom refineries using the electrolytic processes are in a position to credit the smelter enough for copper in bullion to discourage the skimming process. For these reasons it may be expected that the tendency will be toward more copper in the bullion, and not less, so that the consideration of bullion carrying more copper, from  $\frac{1}{2}$  to 1% or more, is important.

Probable cost of treating slime by (2c), from lead bullion containing per ton 20 lbs. antimony, 10 lbs. copper, 5 lbs. arsenic, and 70 ozs. of silver, beside which 5 lbs. of lead remain in the slime:

TABLE 80.

	Per Ton Lead.
Sulphuric acid lost, 15 lbs. ....	\$0.12
Hydrofluoric acid lost. ....	0.08
Operation electrolytic tanks, including power at \$50. ....	0.48
Power, 140 K.W. ....	\$25.60
Labor. ....	7.50
Repairs. ....	2.50
New anodes. ....	12.20
Per day (100 tons) ....	<u>\$47.80</u>
Repairs and supplies. ....	0.10
Melting and refining doré at $\frac{1}{2}$ cent per oz. ....	0.14
Labor not already included. ....	0.18
Coal. ....	0.05
	<u>\$1.15</u>

If bismuth is present it will be recovered from the sediments deposited from the sulphate solution, and from the doré bullion, at small cost.



(2d) This process gives a similar result and is a little inferior, though the loss of sulphuric acid is less. On the other hand the roasted product is not so readily leached, and some sodium nitrate is required to finish the oxidation.

(2e) Ferric sulphate process, for same bullion as assumed for (2c):

TABLE 81.

	Per Ton Load.
Operation of electrolytic tanks, including power at \$50 per year. Copper tanks operate at 1.75 volts and antimony tanks at 2.9 volts, with 90% efficiency each. ....	\$0.63
Power, 175 K.W. ....	\$32.40
Labor. ....	10.00
Repairs. ....	12.50
New anodes. ....	8.00
Per day (100 tons) ....	<u>\$62.90</u>
Hydrofluoric acid loss, 1 lb. at 7.5 cents. ....	0.08
Sulphuric acid, 10 lbs. ....	0.08
Melting and refining doré at $\frac{1}{2}$ cent. ....	0.14
Labor not already included. ....	0.24
Repairs and supplies. ....	0.10
Coal for melting, roasting matte, melting antimony. ....	0.03
	<u>\$1.30</u>
Credit for 30 lbs. copper recovered from matte. ....	1.05
Cost. ....	<u>\$0.25</u>

If bismuth is present, it will be recovered in a special bullion from smelting the leached matte, and to a small extent in the doré bullion.

The above results do not include superintendence and assaying, metal losses, or interest on plant, but the comparison is still valid.

In a general way, the ferric sulphate method, beside being the most economical in net operating cost, is the cleanest, easiest, and quickest, and will cause less loss of precious metals through the various channels of loss, for the slime is not dried at all until the final melting to doré bullion. The ferric sulphate method will recover all the precious metal values shown by corrected fire assay, or more.

## CHAPTER VII.

### REFINERY CONSTRUCTION, OPERATION, AND REFINING COSTS.

THE general arrangement of most, if not all, large electrolytic copper refineries is on the one level plan with industrial railway running between the different departments, motive power being generally provided by electric locomotives. This arrangement can be safely copied for electrolytic lead refineries. In the casting plant the molds to receive melted metal may be on a level a few feet below the general level; but in stacking the anodes, ready to be carried off by the tank-load by the electric cranes, they can be easily hoisted the necessary few feet.

In considering the level question, the tank-room can be regarded as receiving and delivering material on the same level.

The melting plant should be so situated and arranged that lead and bullion may be handled from and to the railroad cars as simply as possible. In order to deliver the cast anodes and pig lead on nearly the same level as the tank-house and shipping track, it is preferable to have the melting-furnaces at a higher level, so that the metal may flow by gravity through siphons to the molds. If a Rösing steam pump is used, the pots may, of course, be brought down to the same level; but



this has been tried at Trail and I believe not found entirely satisfactory.\*

The melting of the bullion bars and anode scrap and of the cathodes has been done up to the present by simple melting down in kettles. The cathodes are wet when they come from the refinery and have to be dried before coming into contact with melted lead in the pot. The usual plan is to pile the cathodes high above the pot and melt down slowly. A cover and pipe should be provided over the kettle to carry off fumes. When the lead is melted finally about 4% of dross floats on top, which is skimmed off by hand, a slow and laborious method. A Howard skimmer, such as used in the Parkes process, to take off the dross, would be a desirable adjunct. Plate 4 shows the Trail melting plant, 1903-1904.

The dross ordinarily produced is less pure than the lead and contains more silver. Table 82 shows the comparative analyses of lead and dross from the same meltings at Trail.

TABLE 82.

	Fe	Cu	As	Sb	Zn	Ag. Ozs
Lead. ....	.0010%	.0003%	.0002%	.0010%	None	...
Dross. ....	.0016%	.0005%	.0003%	.0016%	"	...
Lead. ....	.0008%	.0009%	.0001%	.0009%	"	.24
Dross. ....	.0011%	.0010%	.0008%	.0107%	"	...

I believe that the present method of melting the cathodes is capable of considerable improvement, along the line of saving labor, and making little or no dross. The piling of the cathodes above the pot, and the necessity of steering them

\* See, however, description of lead pumps in Appendix I.



PLATE 4.

TRUSWELL ANODE MOLD AND ANODE.

*page 199*





into the pot properly as the charge settles down, requires some labor, as does the handling of the dross. What is wanted is to dump the damp cathodes by the carload and have no more labor involved until the lead is cast. This end could be achieved by dumping the cathodes through the roof of a preheating reverberatory furnace at a level just above that of the refined-lead kettle. The reverberatory could have a cast-iron or steel bottom to prevent its being broken up by the falling lead.

A very small heat supply will suffice to melt lead in this way, and if the furnace gases were kept reducing at the same time, little or no dross would be formed from oxidation of the melting cathodes. At 50% heating efficiency, which does not seem high for a furnace working at the melting-point of lead, 8 lbs. of coal would be theoretically required to melt a ton of lead. The waste heat from the bullion or refined-lead kettles could be applied very easily to the melting in the reverberatory. A similar operation is the liquation of bullion in a reverberatory, to soften it for the Parkes process, which requires with a 35-ton furnace 24 lbs. of coal per ton of lead melted.\* The objection might be raised that the resulting lead will be slightly less pure, which is undoubtedly a fact. Electrolytically refined lead usually contains from .1 to .5 ozs. of silver, which is in practical work almost entirely due to slime not washed off the surface of the cathodes. In taking a crop of cathodes from a tank, the disturbance of the tank or unavoidable contact of the anodes and cathodes, is apt to loosen some slime from the anodes and get part of it on the cathodes. When these are dipped in muddy wash-water, as

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\* Collins, "The Metallurgy of Lead," page 288.

is sometimes done, the result is an even distribution of part of the slime over the surface. In the ordinary melting quite a little of this slime goes into the dross, as will be seen from Table 83, from the United States Metals Refining Company.

TABLE 83.

Lead.....	.25	ozs. per ton.
Dross 20 mesh oversize.....	1.836	" " "
" 40 " " .....	1.776	" " "
" 60 " " .....	1.75	" " "
" though 60 mesh.....	3.66	" " "

Assuming 4% of dross reduced and melted into the lead, the lead would have carried approximately .35 ozs. instead of .25 ozs. of silver, provided all the adherent slime was taken up by the lead, which is not probable, as some of the slime would probably remain in the furnace as dross. The difference in the amount of the other impurities in the lead would be too small to be noticeable.

For a combined smelting and refining works, the lead should be cast from the blast-furnaces into anodes direct.

In refineries, anodes are cast in open molds lying in a semi-circle in front of the pot, to which the usual lead launder reaches from the discharge end of the siphon or pump. These may be seen mounted on a long car in the photograph of the Trail melting plant of several years ago, Plate 5.

The use of a rotating table, on which the molds are placed, similarly to the casting machinery used in electrolytic copper works, has been proposed, but it is doubtful if it would save anything in cost of casting. It is quite possible that the adoption of rotating molds in casting copper anodes was a necessity, because copper could not be conveniently run through a long launder to a semicircle of molds, and copper requires





fied. Once in a while the anode molds should be sprinkled with clayey water, which rapidly dries off the hot iron, and leaves a coating to which the lead cannot stick. The block at the top between the two lugs is separate and removable, and gives a place to put a bar in to lift the anode slightly from the mold, so that it may be engaged by hooks. A compressed-air hoist on a light jib-crane enables one man to lift anodes and stack them rapidly.

The anodes molded in the way mentioned suffer from irregularities of form or weight, as would naturally be expected when the workman's sole means of judging the amount of metal run into each mold is by eye. Then the molds and inflowing bullion are at various accidental temperatures, so there can be no uniform procedure for getting the right amount of metal in the lugs and all the different portions of the plates. Even if the mold is perfectly level an anode may average considerably thicker on one end than the other from the unequal flow and chilling of the lead. When these irregularly-formed plates are suspended in the tanks the thinnest plates will be entirely dissolved, while considerable metal remains on some of the others, increasing the proportion of anode scrap to be remelted. A stiffening rib about  $\frac{1}{4}$  inch deep and 2 inches wide is usually cast across the top of the anodes to prevent their collapsing and falling in the tank at the end of the run when the metal has been nearly all dissolved. Part of the rib, of course, remains when all of the lower part of the anode has been decomposed.

For the best work and highest efficiency in the tanks, the anodes should all be of the same weight, and slightly thicker at the top than at the bottom. For these reasons the idea of using closed molds for casting the anodes has been an attrac-

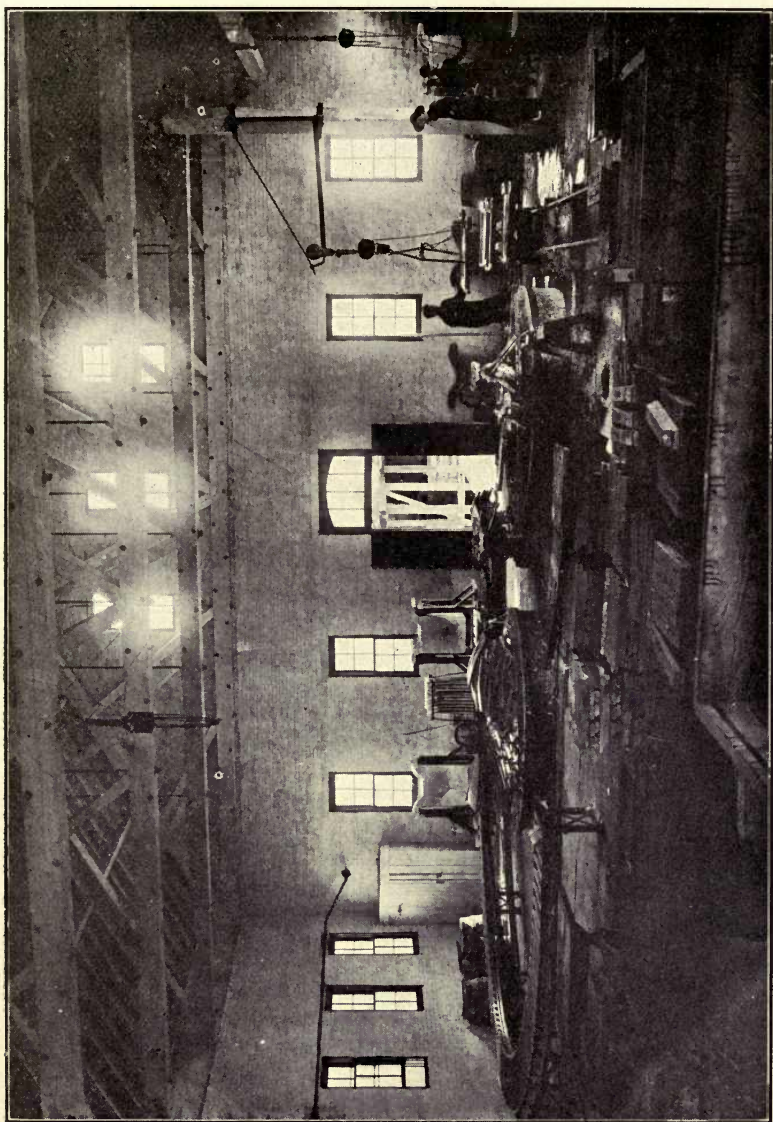


PLATE 5.

LEAD CASTING PLANT, 1903.

Consolidated Mining and Smelting Co. of Canada, Ltd., Trail, B. C.







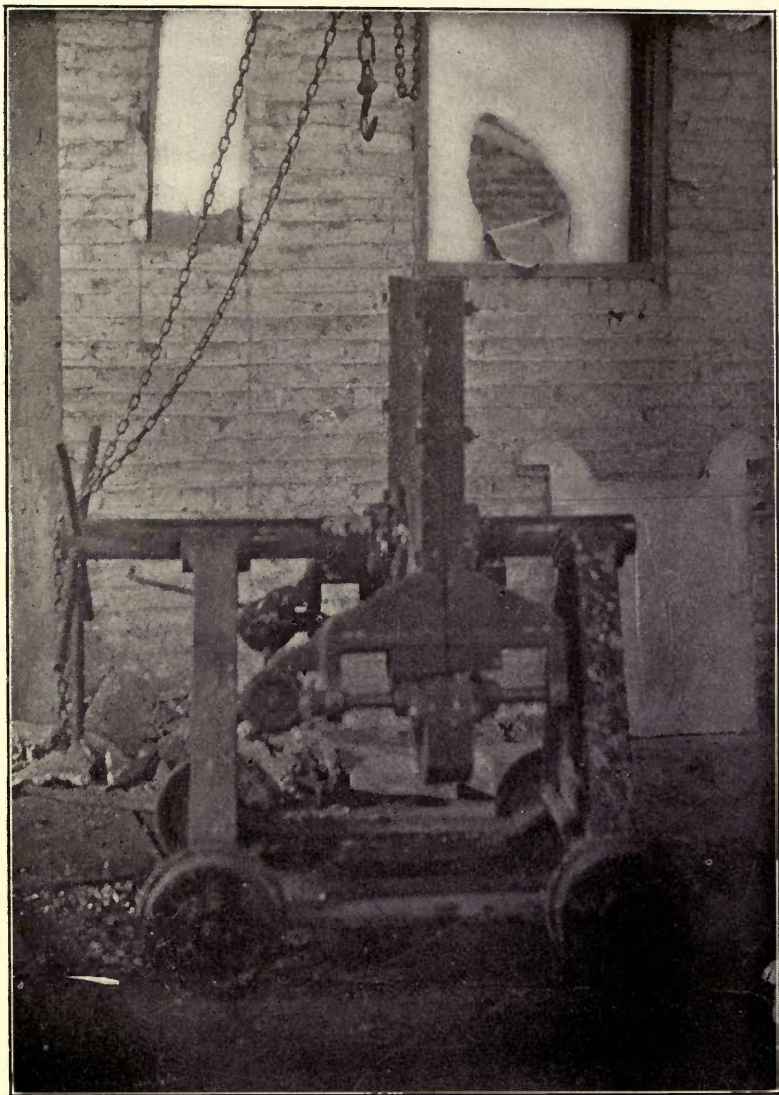


PLATE 6  
TRUSWELL ANODE MOLD



tive one. The closed molds should aim preferably to cast the anodes bottom up so that the dross rising in the cooling liquid metal can not flow into the lugs, both weakening them and sending the impurities back to the melting-kettle in greater relative amount than they exist in the bullion. With anodes cast in closed molds experimentally, the tank efficiency has been raised at Trail to 95%,\* as against the usual 90%. Mr. R. Truswell, Trail, B. C., has applied for United States,† Canadian, and English patents for his anode-mold, which is shown in the photographs supplied by Mr. Truswell, Plates 5 and 6. The following description is from Mr. Truswell's article:‡

"The illustrations show a new mold that I have developed for the purpose of casting anodes; it has the advantage that the plate, being enclosed during the process of casting, will be of uniform thickness and not liable to be warped or twisted. To prevent the dross or spongy characteristics found in some plates it is cast on end, and under a head of fluid metal to ensure its soundness. The dross rises toward the gate, and, as this is near the lower end of the plate, its defects are less noticeable than when the method of pouring is not that specified.

"In the illustrations, Figs. 30 and 31, are profile views of the plates for which the construction of the mold is adapted. Fig. 32 is a front elevation of the mold mounted as for pouring. Fig. 33 shows a cross-section on AA in Fig. 32, and Fig. 34 is an end elevation of the mold, inverted after casting and with the mold opened for removal of the cast plate. Fig. 35 is a detailed cross-section of the slide and nut of

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\* Communicated, Mr. W. H. Aldridge.

† United States Patent, 823977. June 19, 1906.

‡ *Engineering and Mining Journal*. May 5, 1906.



the opening portion of the mold, and Fig. 36 is a detail section showing a modified form of joint between the head and plate portion of the mold, by which the parts which enclose the head are sustained when inverted.

“The anode plate is represented by 2; that shown in Fig. 1 is provided with laterally projecting horns, 3, by which the plate is supported on the walls of the tank; that shown in Fig. 2 has eyes, 4, which are usually bent and cast into the plate, but may be cast with the plate.

“The main body or plate portion of the mold is formed of two recessed parts, 5, secured by any suitable fastening, so that the recesses when together will leave a space 6, to form the mold of the lower or uniform portion of the plate. These recesses are carried to the end of the mold, so that the metal may be poured from that end which forms the lower part of the plate when in position in the tank.

“The head of the plate, including the horns, 3, or eyes, 4, as the case may be, is formed by two portions, 7, each having recesses, 8, to form the desired width and shape of head which they entirely enclose. These portions, 7, are slidable outward from the middle plane of the mold a sufficient distance to clear the mold from the projecting portions of the plate which has been cast within it. The contiguous edges are beveled as at, 8, so that they will form a close joint together.

“Each drawback portion, 7, is furnished on each side with outwardly projecting members, 9, by which they are supported on V-shaped slides, 10, on brackets, 11. These project from the adjacent sides of 5, and the parts, 7, are slidable to or from the plane of division by screws, 12, having right- and left-hand threads on their opposite ends. These pass respect-

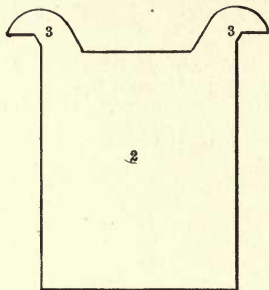


FIG. 30.

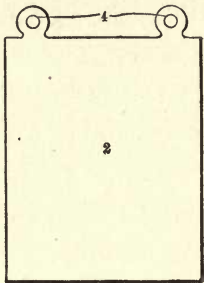


FIG. 31.

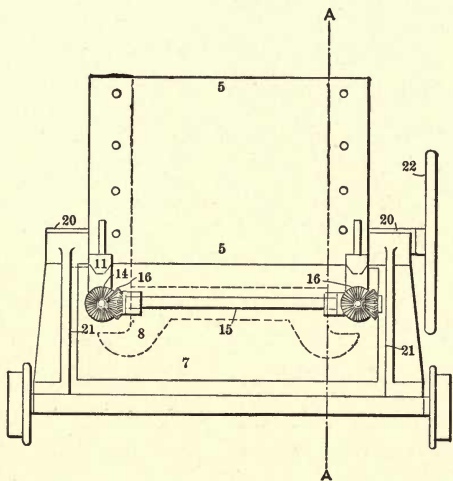


FIG. 32.

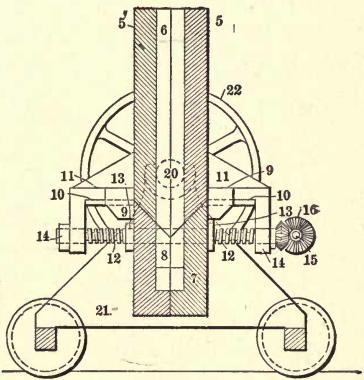


FIG. 33.

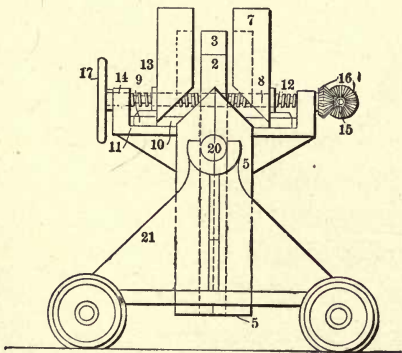


FIG. 34.

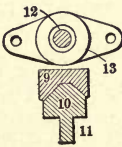


FIG. 35.

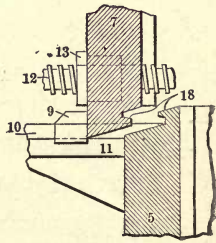


FIG. 36.

ively through corresponding nuts, 13, secured by screws to the parts, 7. The screws, 12, are supported in bearings, 14, upwardly projecting from the outer ends of the brackets, 11, and are rotatable therein by a hand-wheel or crank, 17, on either one. A shaft, 15, extended between the screws and connected to them by beveled pinions, 16, enables them to be simultaneously operated.

“The mold is pivotally mounted by trunnions, 20, secured to or forming a part of the plate portion, 5, in a frame, 21, provided with wheels; it is furnished with a hand-wheel, 22, by which it may be inverted in the frame.

“In operation the parts, 7, are tightly closed and the mold is inverted to bring the open end of it uppermost as in Figs. 32 and 33. The metal is then poured in, and when set the mold is again inverted, the parts, 7, withdrawn, as represented in Fig. 34, and the plate drawn from the mold. Some draft may be desirable in the width and thickness of the plate, towards the open or pouring end of the mold, to facilitate its removal. It may also be necessary to support directly the head-end members, 7, when the head mold is closed, to enable them to sustain their weight and that of the fluid metal within the mold. For this purpose some such modification as is shown in Fig. 36 may be adopted. In this engaging lips, 18, are provided on the contiguous edges of 5 and 7, the lips securing these parts of the mold against separation endwise.

“These molds can be made with water-jackets, and can be mounted on cars in any number desired, and can all be opened at once by the turning of one lever.”

The molding of the refined lead calls for no special remarks, the usual method described by the authorities on lead smelting being used.



The sampling of bullion bars received to be refined, would be done in the ordinary manner, taking five punches diagonally across a row of five bars on the top, and then turning them over on the bottom and taking one punch each from each bar in the same manner, but on the opposite diagonal.\* Sampling anodes does not give the same result as is got from the bars from which the anodes were cast, and both are lower than a dip sample taken from the lead flowing to the molds. I believe the sample taken by punching anodes in a small number of places can be relied on very closely, for usually in casting the lead chills in the anode mold pretty quickly, especially in the lugs and corners, and you have a plate of comparatively small and even thickness to punch several times on both sides. The following results in Table 84 are from a test made at Trail, July, 1902.

TABLE 84.

Sample No.	Bar Sample		Dip Sample Anode.		Punch from Top Anode.		Punch from Bottom Anode.		Average Top and Bottom.	
	Au	Ag	Au	Ag	Au	Ag	Au	Ag	Au	Ag
1	2.79	322.2	2.88	328.6	2.72	316.0	2.84	324.7	2.78	320.7
2	2.91	331.1	2.92	333.6	2.90	329.6	2.99	331.6	2.94	330.6

**Size of tanks.**—This will have to depend on the capacity of the plant. For fair-sized or large plants a current of 3500 to 6000 amperes is satisfactory, the latter probably being more favorable. It seems evident that the larger the tanks can be made the smaller the cost of tank construction and

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\* Hofman, "Metallurgy of Lead," 1899, page 351.

maintenance per ton produced. The separation of electrodes, which is usually expressed in distance from center to center of anodes, varies from  $4\frac{5}{8}$  to  $4\frac{15}{16}$ '' as follows:

TABLE 85.

Trail, B. C.....	4.375 inches.
Grasselli, Ind.....	4.625    "
Newcastle-on-Tyne.....	4.15     "

The anodes are about 3 to 4 inches narrower than the tanks themselves. The anode width is usually about 2 feet, but this can be increased as well as not to 2 feet 6 inches, or even 3 feet, and thereby shorten the tank and reduce the number of electrodes to be handled.

TABLE 86.

Plant.	Anode Width.	Tank Width.
Trail, B. C.....	26 inches	30 inches
Grasselli, Ind.....	24    "	30    "   probably.
Newcastle-on-Tyne...	33    "	37    "

The depth of the anode exposed to the electrolyte is from 2 feet 10 inches to 3 feet.

TABLE 87.

Plant.	Anode Depth.
Trail, B. C.....	34.5 inches.
Grasselli, Ind.....	36    "
Newcastle-on-Tyne.....	34    "

Adopting the maximum dimensions now used in each case for a 6000-ampere current, anodes 33 inches wide and 36 inches deep, current density 17.5 amperes per square foot, space center to center of anodes  $4\frac{1}{2}$  inches, the tank would need the following dimensions inside: length 8 feet, depth 3 feet 9 inches, width 3 feet 1 inch.

Wood tanks have been used exclusively, for which Southern yellow pine is good material. Cedar was tried at Trail first and found rather soft, and more recently better results have been obtained with fir.

The tank of the future, in my opinion, will be made of reinforced concrete, saturated with sulphur by immersion in a sulphur bath.\* They are cheaper than wood and absolutely acid proof. A small tank of this kind in my laboratory containing hydrochloric acid is in the same condition after several months' standing. There is absolutely no action of the acid on the tank. Other tanks are now being tested on a practical scale, with good results, as far as corrosion goes, though they cracked somewhat in the corners.

The preparation of a concrete tank of any particular size and shape, reinforced or not, does not need any very long description here. An article by Mr. D. H. Browne † gives a good description of the manufacture of electrolytic tanks, from which the following remarks are taken:

“The first requisite is a good, slow-setting cement. Slowness of set is necessary because in building large tanks it requires ten or twelve hours or even more to carry up the walls to the required height, and as the ramming must be continuous throughout this entire time, it is evident that if the bottom took its initial set before the sides were completed it would be injured by the vibration. The cement, therefore, should take longer to set than the tank to complete. Cheap cement is worse than useless. Saylor's cement has proved a reliable

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\* Patent applied for.

† “Electrochemical and Metallurgical Industry,” Vol. I, page 273.



article, but any brand which will stand the 'pat' test will be satisfactory.

"The 'pat' test is made by mixing a handful with water to a stiff paste and working the same on a glass plate into a cake about half an inch high and 3 or 4 inches in diameter. The surface should be troweled smooth and the sides brought down to a thin edge. This is allowed to stand a few hours, then is covered with a wet cloth and set aside in a cool place over night. If it sets slowly and shows no cracks on the surface or at the edges it will answer.

"For the best work crushed granite should be used. This has a rough granular fracture or 'bite,' into which the sand and cement lock better than with any other rock. As the stone used is the weakest part, and as a good concrete, when broken, shows fracture across, and not around the particles of stone, it is important to use the best rock available. Failing granite a trap rock or blue diorite is a good substitute. The size of the rock depends on the thickness of the walls; a safe rule being that no piece should be over one-quarter the thickness of the wall in which it is used. For ordinary tanks material passing through a screen of  $1\frac{1}{2}$  inches and over a screen of one half inch is satisfactory. The material smaller than one half inch should be rejected, as it interferes with the filling of the voids.

"The solidity of concrete depends largely on the care with which these voids are filled. To determine the void space, take a pail of crushed rock, calculate the volume and find the weight. Add now water till the pail is full and weigh again. Calculate the volume of the water and simple proportion shows the empty space between the particles of rock. This space must be filled with sand, of which in turn the voids

must be filled with cement.\* The voids of cement are in their turn filled by the water absorbed. Hence for strong concrete the common use of the formula, '4 parts rock, 2 parts sand, 1 part cement.' For less careful work a larger proportion of rock is often used.

"To mix the cement a tight mortar-box or floor and a measure holding one cubic foot are needed. The rock should be thoroughly washed and the sand screened from clay or gravel. One cubic foot of cement to two of sand is mixed on the dry floor to an even composition, and to this four cubic feet of stone are added, and the mass thoroughly shoveled over. Water is now added, so that, while no muddiness is apparent, each particle is moist. The mass is again shoveled over and is now ready for the mold.

"This mold may be of any shape whatever. It is set on a solid floor, with a sheet of building paper underneath so that the tank does not bind to the floor. The sketch shows a form for a commercial-plating bath. The outer frame is trued at right angles and braced by struts to the floor to prevent bulging of the sides under the rammer. The concrete is now shoveled in, a few inches at a time, and thoroughly rammed until water shows at the surface. For a tank of the size shown three men are needed ramming and two men mixing and handling concrete. The tools needed are iron rammers, about 2 inches thick and 3 or 4 inches square, with a sleeve for a wooden handle. Such a tool, handled with a short, stiff blow, is better than a lighter tool, with a springy blow, the idea being simply to drive out the air from between the particles and completely fill the voids.

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\* This method of test not now considered entirely correct.

“As soon as the bottom is of the desired thickness the inner frame is put in place and braced by cross-pieces to prevent inward bulging. The sides are now rammed up, a few inches at a time. It is not desirable to lay the sides in layers, but rather to carry them up without coursing or stratification. One thing is very important—that there be no stoppages. If a mealtime intervenes the men should be relieved one at a time, so that no pause occurs till the tank is completed.

“The top finish is put on by bringing the concrete to within a quarter of an inch from the top of the mold and carrying this up with equal parts sand and cement troweled to a smooth surface. Any openings or holes in the tank wall are made by inserting a block of wood of the desired size in the side walls. After the tank is set the wood can be drilled or broken out.

“Three or four days should elapse before the moldboards are taken down. The inner frame is removed by unscrewing the angle irons shown, when the side boards will drop inward without any difficulty. The outer form falls apart on removal of the the rods. If necessary the inner surface can be finished with a coat of sand and cement, but if planed boards were used for the molds the surface is usually quite smooth.

“Concrete will not stand strong acids; caustic or chlorine has no effect upon it. A coating of paraffine or tar would help it to resist acids. It should not be subjected to sudden changes of temperature. If the heat be brought up gradually it will stand fire. It can be handled or lifted like a block of granite if ordinary care be used to prevent the tools from bearing against the sharp edges of the tank.





REFINERY CONSTRUCTION, OPERATION, REFINING COSTS. 219

“A tank with 6-inch bottom and 4-inch sides, containing 24 cubic feet of concrete, can be set up and completed by five men in one day. The cost decreases with the number of tanks built at one time and the facilities for handling concrete. Building four tanks of this size per day the cost per tank was as follows:

TABLE 88.

Carpenter and blacksmith labor on molds.....	\$1.75
Concrete work labor, 30 hours at 17½ cents.....	5.20
3.5 cubic feet cement at 60 cents.....	2.10
7 cubic feet sand.....	.25
14 cubic feet crushed trap rock.....	3.00
	<hr/>
	\$12.30

“Including finishing, taking down molds, cementing in rubber-pipe connections, about \$15 will cover the cost of building a tank as above described, the dimensions of which are about 3 feet wide, 9 feet long and 2 feet deep. No construction of lead, slate or wood can be made which will fulfill all the requirements of the case for this sum.”

To make the tank acid-proof, after standing moist for several weeks until well set, the tank is dried out pretty well, and then lowered into an iron vessel containing just-melted sulphur. The sulphur is gradually heated to 150° C. or so, but not to the thickening point. This should take quite a number of hours, perhaps 12, steam coming off regularly as long as the temperature is rising, and of course removing with it all permanent gases present in the concrete. The sulphur is then allowed to cool slowly during another 6 to 12 hours, when the sulphur penetrates the crevices and cracks in the concrete. Probably the atmospheric pressure helps

in this, as the reabsorption and contraction of steam in cooling would make a vacuum in the concrete.

The tank is then lifted out, and after cooling to perhaps 80° to 90° C., is quickly dipped in again and taken out. This chills a thin, smooth layer of sulphur on the tank, and fills any cracks, while the coating produced does not come off or crack off during long periods. A coating of asphaltum paint applied later is partially absorbed by the spaces between the sulphur crystals and adheres very well. In fact the surface of the finished tank will soak up quite a little paint, melted paraffine, etc.

Wooden tanks have been built with all bolts clear of the wood and with bolts through the wood. Figs. 37 and 38 show the two methods of construction. The bolts in the wood show corrosion badly sometimes, especially where the bolts pass from one plank to another. Iron is not rapidly attacked by the lead-depositing electrolyte when no current is passing in the neighborhood, but as there are slight differences of e.m.f. between different parts of the tank, it would only be expected that lead would deposit on one part of an iron conductor touching the solution at several places, and iron dissolve at another. For this reason bolts clear of the wood could be expected to last longest. The first tanks at Trail were made in this way, but in the tanks used now the bolts pass directly through the wood. If the bolts could be surrounded by a rubber tube, or copper bolts used, they would then be most successful. The expedient of pouring hot paraffine, pitch, etc., through the holes before putting in the bolts, seems to help a little, but not to be entirely successful. In designing a wooden tank, the placing of the bolts should be studied not only from the mechanical standpoint, but to reduce elec-

trolytic corrosion of the iron as far as possible, which I am satisfied is the main cause of the failure of the bolts.

As an example, if two tanks are bolted together, as shown in Fig. 39, it is evident that the current will tend to pass

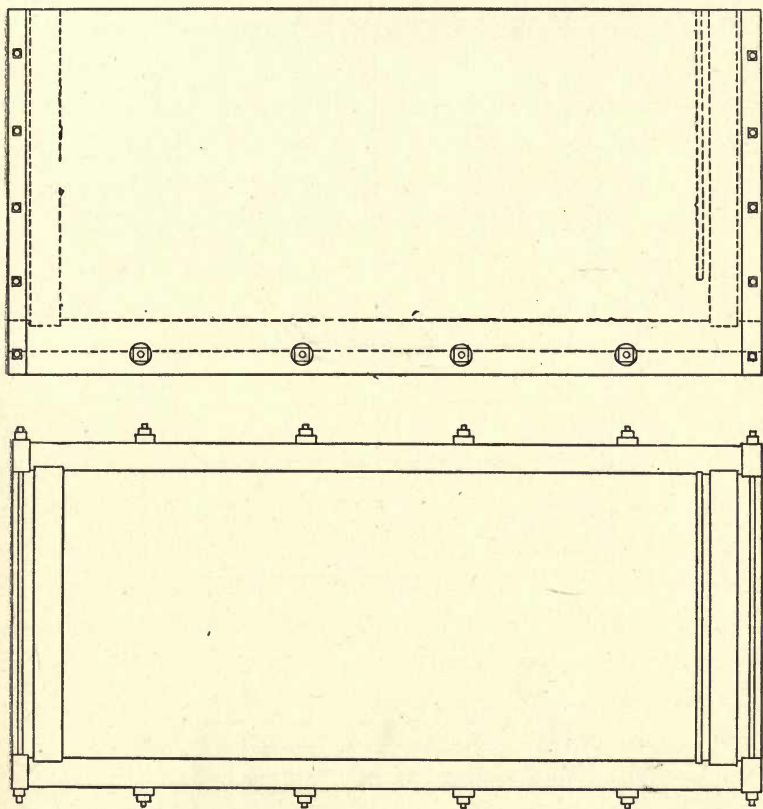


FIG. 37.

through the wet wood to the iron bolt in one tank, depositing lead on it probably, and pass from the bolt to the solution in the other tank, with too rapid corrosion of the bolt. It would be expected that the greatest effect on the bolt would



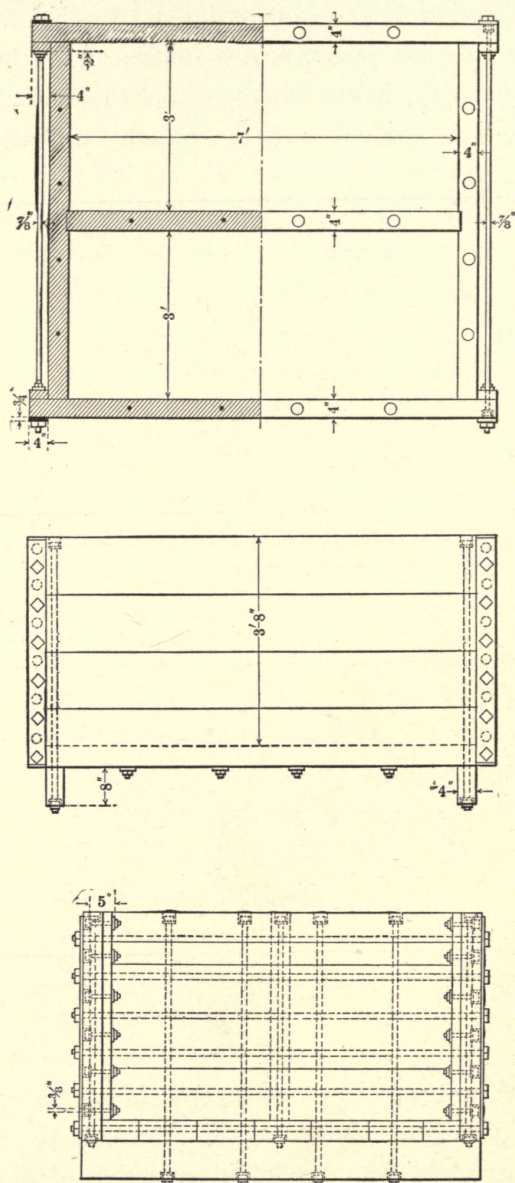


FIG. 38.

be where it passes from one plank to another, unless the joint in the wood were perfect. As a matter of fact, that is where bolts fail usually. Bolts as shown in Figs. 40 and 41 would be apt to carry current as shown, if the tanks rested on a wet beam.

A few tenths of an ampere would cut a bolt through in a moderate time.

Three- or four-inch planking should be used for tank walls and bottom, four inches being best. Tanks with four-inch sides do not need a bolt across the top in the center or braces to hold the sides from bulging. The use of feather and groove in the joints is preferred by some and not by others.

The problems to be settled in connection with the tanks are their arrangement and differences of elevation for circulation purposes. Two general systems of locating tanks for the multiple system are in use both in electrolytic copper and lead refining. The older method, which we may call the "cascade," originated, I believe, by Mr. F. A. Thum, uses double rows of tanks end to end, each pair at an elevation of  $2\frac{1}{2}$ –3 inches above the next pair, while a continuous circulation of solution flows from the highest tank at one end to the lowest at the other. The newer arrangement patented by Mr. A. L. Walker \* offers some important advantages especially for copper refineries, in requiring less space, less copper conductors by far, and saving some power. For lead refining, considering that the number of tanks, amount of conductors and power are only about a third as great per ton produced as in copper refining, it is evident that these advantages are much reduced when the Walker arrangement is ap-

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\* U. S. Patent 687800. December 3, 1901.



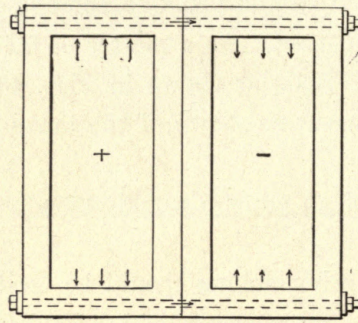


FIG. 39.

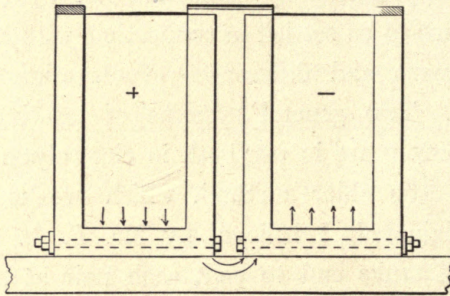


FIG. 40.

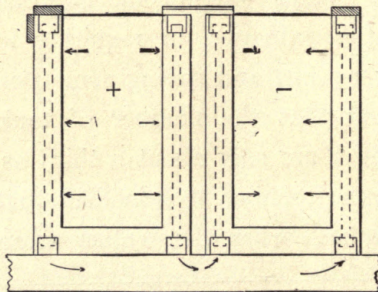


FIG. 41.



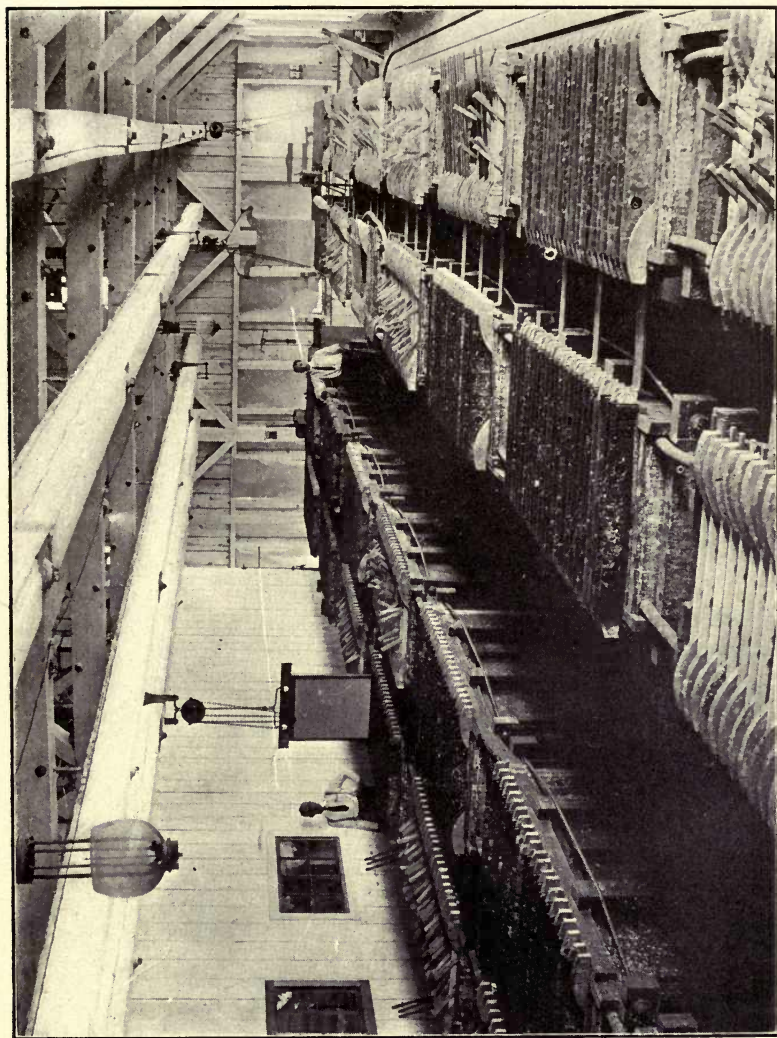


PLATE 7

ORIGINAL LEAD-DEPOSITING TANKS,

Trail, B. C., 1902.



plied to lead, while the disadvantages, which are of a mechanical nature due to greater crowding, are increased somewhat. There is also more chance for injury to the workmen with the Walker system.

The first tanks at Trail, shown in Plate 7, were arranged by the cascade system. The next tanks had the newer arrangement, and the two systems were operated side by side, the old arrangement giving much higher efficiency and better satisfaction. As thereafter more tanks were added according to the old system, it is to be inferred that the old system was considered best. The Grasselli plant of the United States Metals Refining Company uses the Walker system.

The Walker system uses less power and less copper bus bars, which latter may be taken to be about \$50 less per ton per day installed in first cost of copper. The saving in space would not amount to over about 80 sq. ft. of area per ton of lead per day, as the tanks are usually installed; worth say \$80 per ton refined per day. The power lost in the bus bars from tank to tank with the old system, using 5 sq. in. of copper for 4000 amperes, is about 85 watts per tank, or per ton per day, about 235 watt days = 5.6 K.W. hours per ton lead, or 4.3 cents' worth, with power at \$50 per year. A loss of current efficiency of 6% (which may be expected when leaking wooden tanks are placed in two continuous rows close together) would offset this gain. With absolutely tight and non-conducting concrete tanks mentioned on page 23, there would be however no objection from current leaks. The only saving by the Walker system is then about \$130 per ton per day in first cost, and 4 cents per ton in power, a total of about 8 cents per ton, figuring interest on cost for extra copper and extra space as high as 10%.



**Subdivision of tanks into blocks.**—With the cascade system we can have a sloping floor so that the tanks are everywhere at the same height above the floor, which is however not as good as a level floor with tanks at various elevations above the floor. Allowing  $2\frac{1}{2}$  inches drop between the tanks end to end, probably not more than 7 or 8 tanks can be used for each circulation system, making blocks of 14-16 tanks, occupying a space of 6 to 7 feet by 50 to 65 feet. With the Walker system any number of tanks may be placed side by side in one row, the circulation being from row to row, which are at different levels, and not from tank to tank. Four rows are usually arranged in a bay 50 to 55 feet wide.

**Cathodes.**—The first cathodes\* used were of lead-plated sheet-iron. In the use of these cathodes it was noticed that a preliminary plating of copper prevented corrosion of the iron underneath. At Trail a number of tanks were operated for some months with one-eighth inch sheet steel cathodes, but the experiment was not regarded as successful. The cathodes were provided with grooved wooden strips which fitted on their edges, to prevent the growth of lead where it could interfere with pulling the deposits off. The lack of success was on account of lack of sufficient care in the preparation and plating of the sheets. Some of the cathodes which were carefully plated for depositing starting sheets were not attacked, but most of the others were. When not well protected by copper and lead the iron pitted, and the deposited lead was not as hard and solid as when deposited on lead.

On the other hand the labor was much less with the steel cathodes, and there were no short circuits from the anodes

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\* U. S. Patent, A. G. Betts, 679824. August 6, 1901.

and cathodes touching. Had they been carefully plated with copper before lead-plating them, and replated if worn out, their use would probably not have been abandoned. The cost for plant is of course greater with steel cathodes, namely about \$100 per ton refined per day. Those used at Trail were made of tank steel and had to be selected, as some of the steel was too much warped. By stretching, perfectly flat sheets could be produced, and this is an actual manufactured article I am told, though I have not been able to find out where stretched steel sheets are made. A copper bolt was riveted and soldered to the cathode lug to take the current, while the upper part of the steel cathode was painted with P. & B. paint as a protection from acid spattering on them. They were greased before receiving the deposit so that it could be readily removed. These cathodes may be seen in Plate 7. The two round holes were used for lifting.

Usually lead cathodes are used, either of deposited or cast sheets. The first cathodes used at Trail were of deposited lead, made in four tanks six inches deeper than the others, with correspondingly longer anodes and cathodes, the latter of copper- and lead-plated steel. These cathodes had been carefully prepared, and very good deposits of lead were obtained, which were stripped off and wrapped by hand around the copper cross-bars for the other twenty-four tanks. For greasing the steel cathodes a solution of paraffine dissolved in benzine was used. It was found necessary to let the benzine dry off or otherwise the deposited lead stuck fast.

The rough side of the sheet was put next the cross-bar to give better contact, but the contacts were not as good as could be wished. At one time clips were put on the cathode

bars to try to improve the contact, but this was not worth the trouble. The clips may be seen in Plate 7.

A great many plans were suggested for casting thin cathode

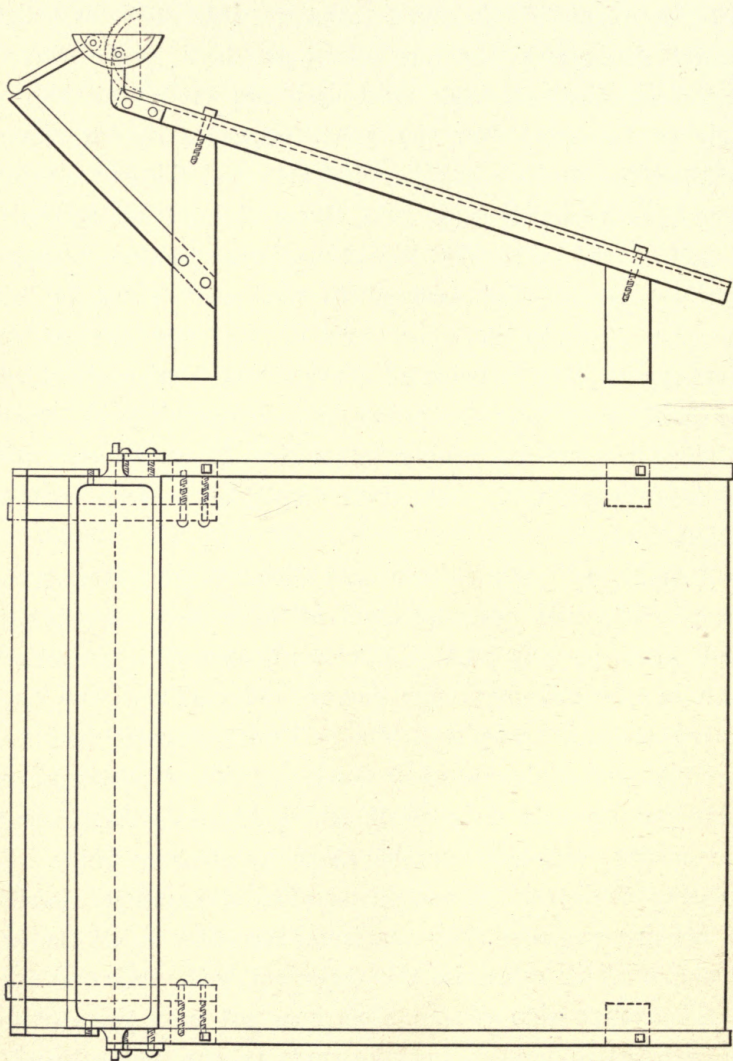


FIG. 42.



sheets, including rolling, dipping cold iron plates into melted lead, revolving a cooled steel drum in a lead pot, and rolling up the resulting lead strip to be afterwards cut into lengths. Mr. John F. Miller, of the Canadian Smelting Works, brought out the apparatus used at present. Pure lead is kept just melted in a small pot and ladled into a pivoted trough at the upper end of a sloping iron plate (see Fig. 42). The lead in the trough is then tipped on the plate, where most of it solidi-

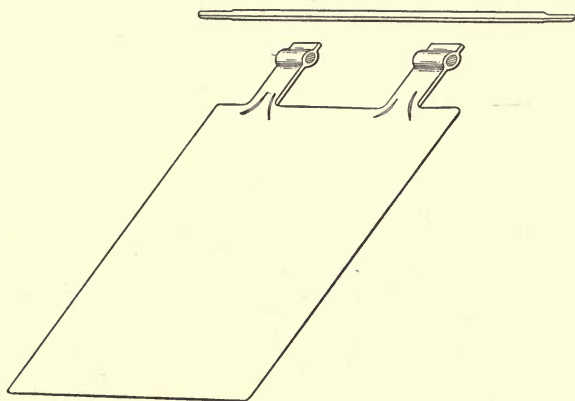


FIG. 54.

fies in a thin even plate, while some is thrown off at the bottom. These sheets are then thrown on a pile, and later on wrapped around the cathode cross-bars by hand.

Dr. Wm. Valentine has improved this cathode by casting two lugs on at the bottom of the plate at the same time the plate itself is cast, using suitable molds in connection with the plate. His cathode is illustrated in Fig. 43. The cathode rod, which is round except where flattened at one end for contact with the bus bar, is inserted in the holes in the lugs. Fig. 44 explains the operation of the apparatus used.

This gives a suspension from the center of the cathode bar, while by the old method the lead is suspended from one side, and the rod has to be kept from turning when resting on the tank and being carried by the crane, by giving

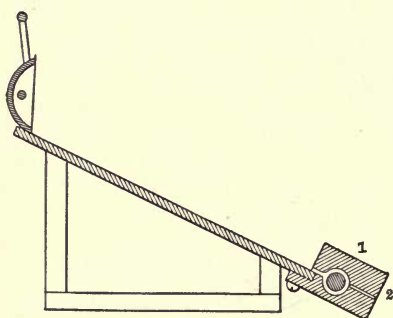


FIG. 44.

the rod a special shape, and using a special hook on the crane (see Fig. 45). The contact with the Valentine cathode is almost perfect, which is a further advantage.

The lead cathodes are all too flimsy and require straightening before use, and careful handling to the tanks, and then there are sure to be short circuits. In tanks where no short

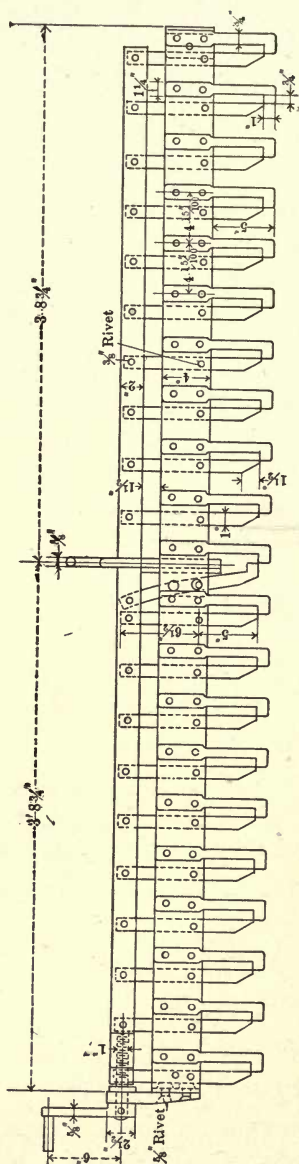


FIG. 45.

circuit actually exists, the uneven spacing of the electrodes causes the anodes to dissolve unevenly, which is a bad thing for a number of reasons. Methods that will insure an even spacing of electrodes and uniform contacts are worth striving for in electrolytic refining.

**Cathode bars.**—These are usually of copper. At Trail rods  $\frac{1}{2}$  inch  $\times$  1 inch on edge were found strong enough. The two ends were twisted flat and offset one half inch at the same time, as shown in the sketch, to prevent the cathode sheet from turning the rod. See Fig. 46. These rods weighed about

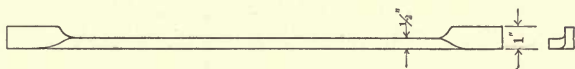


FIG. 46.

6 lbs. each. As  $\frac{1}{2}$  sq. in. of copper is more than necessary to carry 200 amperes, and copper is so much softer than steel, a combination rod is cheaper and better. Steel tubing plated with copper about  $\frac{1}{16}$ -inch thick is also in use. The plating can be readily done by any electro-chemist or plater of ordinary skill.

#### **Tank foundations, supports, and arrangement to catch leaks.**

—Brick piers of sectional area corresponding to their height, with a concrete base, and glass plate half inch thick on top for insulation, make good supports. Concrete is also good. A good way of placing the tanks relative to the piers, for the cascade arrangement of tanks, is not to have the piers under the tanks, but under the aisles between the tanks, while the tanks are carried on heavy cross-beams. See Fig. 47. By cutting a small notch from the beams near the piers, any acid solution is prevented from running down the piers into the ground. It is more difficult to collect any leaks on a



vertical support than that which drops free on the sloping boards underneath.

**Cleaning tanks.**—The usual plan in a copper refinery is to have apparatus arranged so that the slime can be sluiced out of the tank. In a lead refinery the conditions are different,

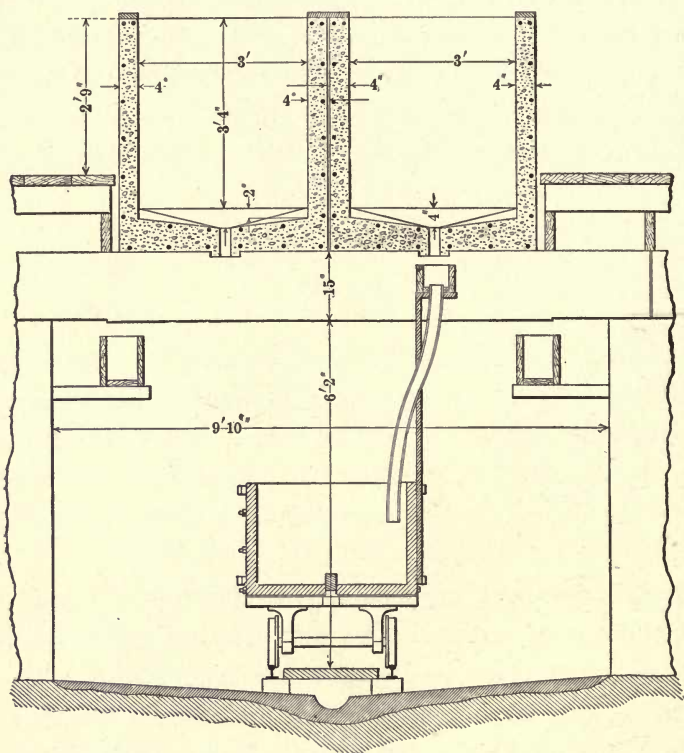


FIG. 47.

for the lead slime is denser and heavier, and generally only a small proportion drops from the anode anyway, and it is often removed in a separate cleaning tank. At Trail we tried the plan of sluicing slime into a tank car in the cellar, but the apparatus was not well arranged, and the slime was too thick to

run out. For this method of removing slime, which has a good deal to recommend it, a tank with hopper-shaped bottom ought to be used. This is difficult to make of wood, but there would be no difficulty in making a concrete tank with such a bottom. See Figs. 47 and 48.

The usual method of emptying a tank is to take out the cathodes first and then the anodes. The clear solution is

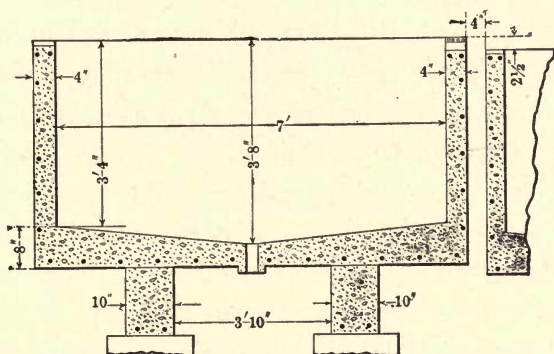


FIG. 48.

next siphoned off into the launder leading to the low-level storage tanks, and the slime shoveled into a barrel, while the tank may next be cleaned with a sponge.

On the method of cleaning tanks adopted depends the height of the cellar. In one case there must be head room in the cellar, the expedient of sluicing the slime all the way to a common collecting point requiring too steep a pitch, so tank cars must be used which can be run under any tank. This means a more expensive plant for excavation and pillars, but it has the advantage of diminishing labor cost, and the tanks can be washed absolutely clean. When electrolyte is added to a dirty tank the slime present is stirred up and set-

bles slowly, and a good proportion may be expected to settle on the cathodes. The sluicing method will give therefore the best results, and the extra first cost is not very great. For relatively impure lead, containing say 2% of antimony and arsenic, the slime remains so firmly attached to the anodes that little or no slime falls into the tanks anyway, and in this case the simplest plant will be equally as easy to operate, on account of much less frequent cleaning being necessary.

An arrangement with track underneath for carrying slime out is shown in Fig. 47. The only sure way of getting the slime to run is to have it drop directly, so the tank car should be run directly underneath the tanks.

Floors of a mixture of asphalt and barite are used and are expected to be solution-tight, but it is doubtful if an entirely solution-tight floor can be made in this way. There are nevertheless some excellent and cheap materials available for catching the leaks. Ordinary tarred roofing paper, supported on boards, is good, and so is roofing paper that has been soaked in paraffine. The solution has no effect whatever on the latter. The experiment has not been tried, but I feel sure it would be successful to cut building paper into squares, soak them in paraffine, and lay the squares like shingles on a nicely prepared sloping surface, either of the ground itself, or the same lightly cemented.

The slime-car arrangement adds to the construction cost, as can be readily seen, for extra height and weight of pillars, excavation and tracks, by an amount which would probably be about \$45 per ton per day. Nothing is included in this estimate for tank car and haulage apparatus, as this substitutes for other apparatus in the other plan. Capitalized at 10% this would be 1.3 cents per ton, while the labor and



time saved, beside making better lead, would be several times that much.

**Contacts.**—The plain copper to copper surface has been tried and found best. Other methods have been tried and given up. Mercury contacts are not good. The mercury disappears rapidly and is probably absorbed by the copper. If the copper contacts are sand-papered off, the drop in e.m.f. will average about 0.01 volt copper to copper, or copper to lead anode. For the anodes, letting the anode lug rest directly on the copper bus bar, gives a very good contact. The under side of the anode lug must be cast flat in order that the anode shall hang straight, and this at the same time makes it certain that it will hang straight.

**Circulation of electrolyte.**—A heavier solution continually falls from the anodes when in action, while a lighter

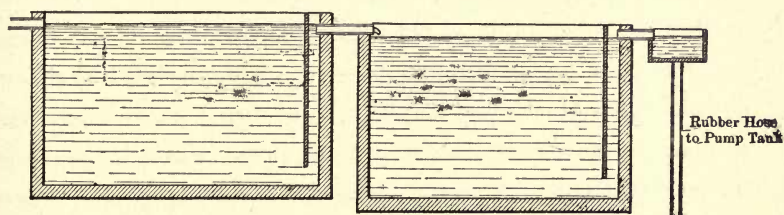


FIG. 49.

solution rises at the cathodes. Depositing 35 lbs. of lead per hour in a tank causes quick decomposition into a heavy layer on the bottom and a light one on top. If the current is shut off, and the anodes have a layer of slime attached, heavy solution diffuses from the slime for some time afterward. The general method of circulation from tank to tank with the cascade arrangement is illustrated in Fig. 49. Rubber hose  $1\frac{1}{4}$  inch internal diameter is fitted in the overflow end of

one tank and rests in a notch at the inflow end of the other. An apron of three-quarter inch wood with a half-inch to one inch space between it and the end of the tank, insures that only the heavy solution at the bottom of the tank can overflow to the top of the next. Some trouble has been experienced by the wooden apron shrinking and opening its seams so that lighter solution can run through. The use of hard-rubber tubes has been attempted in place of the aprons, but I do not know whether it is so successful in preventing the agitation or suction of slime. My idea in using the aprons originally was to have a very slow motion of electrolyte at any one place. A hard-rubber tube takes up as much distance from the end of the tank as the apron, and the objection to cracks opening in the apron does not amount to much, for they can be easily calked up when the tank is emptied.

Certain precautions are necessary to keep the tanks from overflowing on account of the heavier solution at the bottom. If the circulation is uninterrupted the difference in level on the two sides of the apron will not be much more than half an inch. If the circulation is cut off, even when the current has been just cut off too, a sufficiently heavier layer may afterward collect (from the diffusion of the heavy solution in the anode slime) sufficient to cause the tanks to overflow when circulation is again started, instead of forcing the heavy solution behind the apron out at the end. It is very inconvenient to have the solution refuse to pass from tank to tank, and about the only thing to do is to take out some electrodes in each tank, or move them to one end, and stir the tank with a stick. It is also possible to siphon off some of the heavy solution at the bottom and let the tank fill with fresh solution. In actual refining the overflowing of the tanks is a

rare occurrence, but the causes should be kept in mind so that it will be rare.

The volume of solution passed through a 4000 ampere tank can not be so small as to allow of the production of much variation in density between top and bottom of the tank, nor too great to prevent the slime from settling. Five gallons per minute is a fair amount. The difference in density between the top and bottom is about 3%, and sometimes about 5% in practice.

Several kinds of pumps have been in use, giving varying satisfaction. Hard-rubber and bronze centrifugal pumps, driven by small electric motors and connected in the circulation system by good rubber hose, are in use and are very good. Hard-rubber plunger-pumps are also satisfactory. Air lifts using two automatically operated montejus, as described in various books, were tried at Trail first, and found to be very poor for the purpose. A wooden plunger-pump was then hastily constructed and installed and lasted for a considerable period with occasional repairs. The pump was a long square box of 2-inch planks about 5 or 6 inches inside, with a square wood plunger, and leather flaps. Solid rubber balls about  $2\frac{1}{2}$ -inch diameter, on a  $1\frac{1}{2}$ - to  $1\frac{3}{4}$ -inch hole, made excellent valves. Iron was used in the construction of the pump, and even in the solution itself it lasted a long time.

Copper may be used in the construction of the pumps, especially when in contact with lead, so a modification of the wood plunger-pump, using a copper tube with lead plunger and lead valve at the bottom, would be sure to make a good pump. Fig. 50. A plunger-pump has the advantage of not churning any air in with the solution, and can be expected to make somewhat purer lead. It is difficult to see how dis-





solved oxygen in the electrolyte could fail to oxidize some slime, thereby dissolving a little antimony which would partly go into the cathodes.

The deposition of the overflow tanks and pumps may be varied, some methods being shown in Figs. 51 and 52. For filling tanks after cleaning out, the arrangement with a storage tank at a higher level from which tanks that have been emptied may be quickly filled, has some advantages, and is

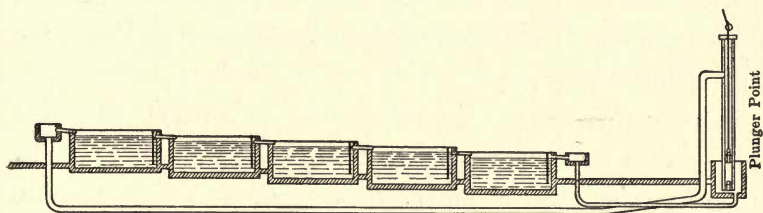


FIG. 51.

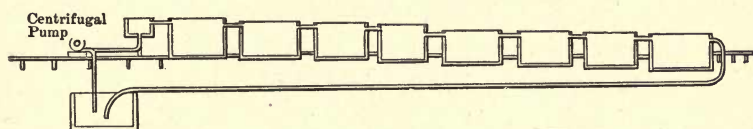


FIG. 52.

probably the best. The other way of letting tanks fill by putting them in the circulation system again, requiring an hour or two to fill a tank, while all below in the same series are without circulation, is not to be recommended.

Considerable storage should be provided for electrolyte from tanks which may be emptied for cleaning. It is convenient with the cascade arrangement to cut out two or four tanks at once; and to provide for two sets of four tanks out, with two to spare, or a storage of say 800 cu. ft., will not be found excessive. Two tanks of 400 cu. ft. each, so that one

can be removed or repaired, would be good practice for wood tanks, and a considerably larger number of sulphur-treated concrete tanks of the same size as the electrolytic tanks would be right for concrete tanks. These latter could be made absolutely tight, and could be connected together by siphons as far as desired, so as to reduce the number of units to be considered to one, with the possibility of always cutting out any desired tank for repairs.

These storage tanks are placed at so low a level that all liquids from the lead tanks, whether by leaks or siphons, run to them by gravity.

There is also to be provided another set of 350 cubic feet capacity at a level above all the tanks so that it may be distributed by hose to any part, with a pump to raise solution from the low-level storage set to the high storage tank.

**Electrolyte.**—The composition of the electrolyte is treated in Chapters I and V. The quantity required, with anodes spaced  $4\frac{3}{4}$  inches center to center, current density 15 amperes per sq. ft., is about 120 cu. ft. per ton deposited per day. If this contains 200 gr.  $\text{SiF}_6$  and 80 gr. lead per litre, its cost is about \$1.25 per cu. ft. as follows:

TABLE 89.

25.7 lbs. fluorspar at \$14 per ton. . . . .	\$0.180
34.7 lbs. 66° $\text{H}_2\text{SO}_4$ at \$12 per ton. . . . .	0.208
29 lbs. fine quartz at \$10 per ton. . . . .	0.145
Coal, 15 lbs. . . . .	0.020
Labor. . . . .	0.220
Repairs. . . . .	0.100
6 lbs. white lead at $6\frac{1}{4}$ cents per pound. . . . .	0.375
	<hr/>
	\$1.248



The yield on fluorspar and sulphuric acid taken is assumed to be only 80% and 92% respectively. The item for repairs is quite large, as lead storage tanks and condensers do not last very well. The cost of the acid itself without the white lead is \$0.87 per cubic foot of electrolyte, or 7 cents per lb. anhydrous  $\text{H}_2\text{SiF}_6$ , the latter item being of interest because  $\text{H}_2\text{SiF}_6$  only is needed for renewals to keep up the strength of the electrolyte. Electrolyte with 160 gr.  $\text{SiF}_6$  and 64 gr. Pb would cost about \$1.00 per cu. ft.

By dissolving lead in the solution electrolytically, instead of using white lead, the cost of electrolyte could be reduced

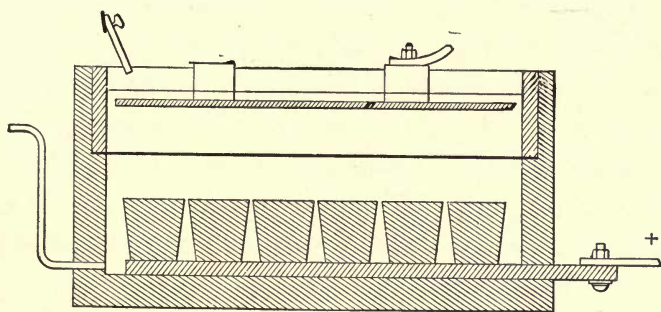


FIG. 53.

by perhaps 10-15 cents per cu. ft. A very simple arrangement of tanks is required, and the power necessary is small, namely, about 25-ampere days per cubic foot. For a 100 ton per day refinery the hydrofluoric acid would be made slowly, requiring say two months or more. The power for dissolving the lead electrolytically could be supplied for example by a 12-volt 500-ampere generator, operating 10 cells in series, putting the necessary lead into solution as fast as the acid was made. See Fig. 53. Current densities of 50 amperes per sq. ft. would be allowable, and the cells would

then be only about 4 ft. square over all. A purer electrolyte to start with may be produced at less cost in this way, and it is therefore to be recommended.

**Washing appliances for electrodes.**—It has been the custom to inspect each finished cathode separately to get off any patches of slime, but these patches come from bad work or crudely cast anodes and flimsy cathodes touching the anodes. This, while excusable in early work, is no longer necessary, so that the inspection of individual cathodes and brushing where slime is attached is no longer necessary when washing. The copper refiners spray a whole tank-load of cathodes at once with hot water from a set of perforated pipes, between which the crane lowers and raises a tank-load of plates. Lead can of course be washed the same way. Dipping cathodes into a tank of wash-water does not give so complete a wash with a given quantity of water and is more troublesome.

Anode scrap may be cleaned before removing it from the refining-tank, by standing over the tank and passing a wiper over the surface of each plate to loosen the slime, provided the slime is uniform and not too hard. With drossy anodes, hard spots are found in the slime that do not come off very easily, and such anodes have been wiped by hand in special cleaning-tanks. For slime which remains attached securely enough to stand removing with the anode scrap (as is usually the case) wiping apparatus, such as shown in Fig. 54, is recommended. This would not work with slime from very hard lead, say 3-10% Sb, as this has to be scraped off.

Regarding the presence of hard particles of slime, this results on one side of the anode only where the dross collects during cooling. This is obviated by the use of closed molds,

and also by casting the lead anodes from the melting-pot at a low temperature, leaving the dross undisturbed on the sur-

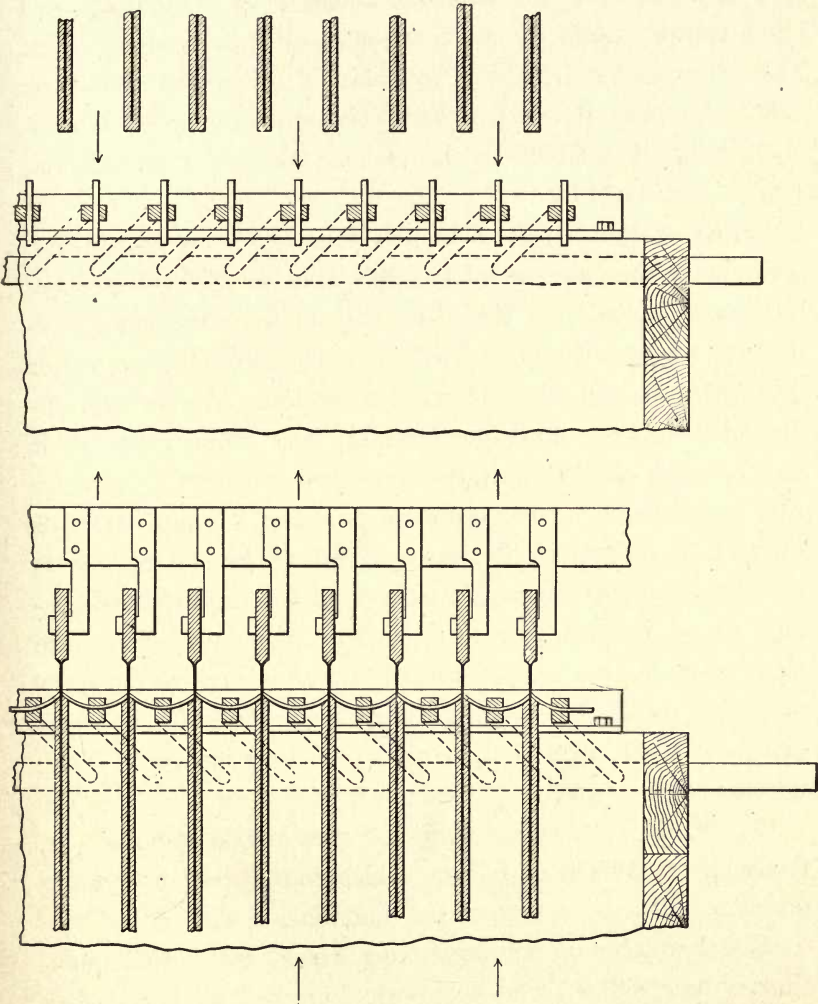


FIG. 54.

face until most of the lead has been cast, and then raising the heat enough to soften the dross so that it may be dipped





into a separate lot of anodes, to be refined in a few special tanks and afterward cleaned of slime by themselves.

After removing the slime the anode scrap is sprayed, dried and melted, while the wash-water is used in washing slime. The wash-water from the cathodes is sometimes used over and over until it nearly reaches the strength of the electrolyte, when it is added to the tanks. For loss of solution involved, see page 39.

**Slime washing.**—The slime, as removed from the anodes, contains a large amount of valuable solution which is stronger and more neutral than the main body of the electrolyte. Filtration and washing has been done by suction filters, filter presses with iron plates, and decantation. The suction filter will probably not come into use any more, although it is successful. The slime filters very well in a press, but there are difficulties in forcing it into a press, on account of lumps of lead that stop up the pipes. Washing by decantation is the best in my opinion. To secure the best result, the washing should be done on the counter-current principle. One washing-tank and several storage tanks for various strengths of wash-water comprise the necessary apparatus, with a steam-pipe to heat the slime and solution, the latter making it break up and wash better.

Mr. F. C. Ryan, of the United States Metals Refining Co., made an experiment as follows, which shows that the heating does not decompose any of the fluosilicic acid.

Equal weights of raw slime were stirred with equal quantities of hot (180° F.) and cold water, for half an hour, when the wash-water was decanted and tested.

As will be seen there was no material difference in the effectiveness of the washing.

TABLE 90.

Cold Water		Hot Water	
Sp. gr. 1.079 = 10.5° B		Sp. gr. 1.083 = 11.0° B	
SiF <sub>6</sub> = 2.95%		SiF <sub>6</sub> = 3.0%	
Pb. = 4.76%		Pb = 4.94%	

Experiment indicates that the slime is readily washed, and no absorption or retention of stronger solution takes place when the slime is stirred up well with water or solution.

I have worked out an equation from which may be closely calculated the effectiveness of washing on the counter-current principle with four washings.

Let  $a$  = percentage of acid in last wash-water

$b =$	“	“	“	“	third	“
$c =$	“	“	“	“	second	“
$d =$	“	“	“	“	first	“
$x =$	“	“	“	“	solution to be washed from	
					slime.	

$$y = \text{ratio of } \frac{\text{volume wet slime after settling}}{\text{Total volume after adding wash-water.}}$$

The equations are:

$$a = \frac{xy^4}{1-3y+4y^2-2y^3+y^4}$$

$$b = \frac{a}{y}$$

$$c = \frac{b-a}{y} + a$$

$$d = \frac{c-b}{y} + b$$

$$x = \frac{a - c}{y} + c$$



If for example one cubic foot of slime is washed with  $1\frac{1}{2}$  cubic feet of water  $y=\frac{2}{3}$ . The acid of the strong solution is about 20%, so I have taken  $x=20$ . In this case, from the above equations:

$$a = 1.52\%$$

$$b = 3.80\%$$

$$c = 7.21\%$$

$$d = 12.33\%$$

This shows a removal of all but 7.5% of the contained electrolyte, or say 1.3 lbs.  $\text{SiF}_6$  per ton of lead. The amount of wash-water to be added to tanks, above the volume of the slime taken out, would be only about enough to make up the normal evaporation in the tanks, taking  $y=\frac{2}{3}$ .

If  $y=\frac{1}{2}$ ,  $a=4.00\%=3.2$  lbs.  $\text{SiF}_6$  per ton lead

$y=\frac{1}{3}$ ,  $a=.64\%=0.5$  lbs.  $\text{SiF}_6$  “ “ “

$y=\frac{1}{4}$ ,  $a=.17\%=.14$  lbs.  $\text{SiF}_6$  “ “ “

$y=\frac{1}{5}$ ,  $a=.06\%=.05$  lbs.  $\text{SiF}_6$  “ “ “

Plant for washing is shown in Fig. 55.

A single plunger-pump can be used for pumping wash-water from the storage tanks to the washing tank. The storage tanks are at a lower level, so the clear solution may be siphoned off directly. The storage tanks are required to hold twice as much as the washing tank.

**Conductors.**—Rolled copper conductors are used, which may be either nearly square in cross-section or flat. The flat



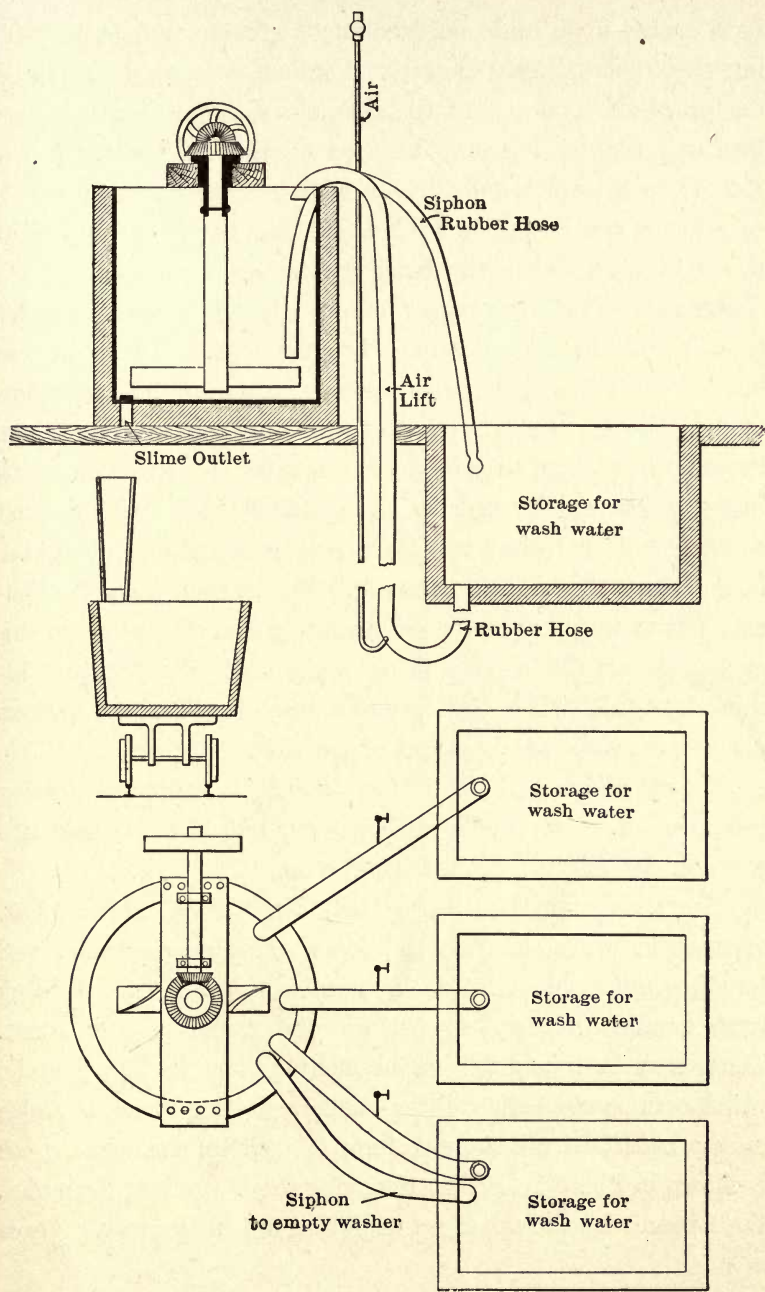


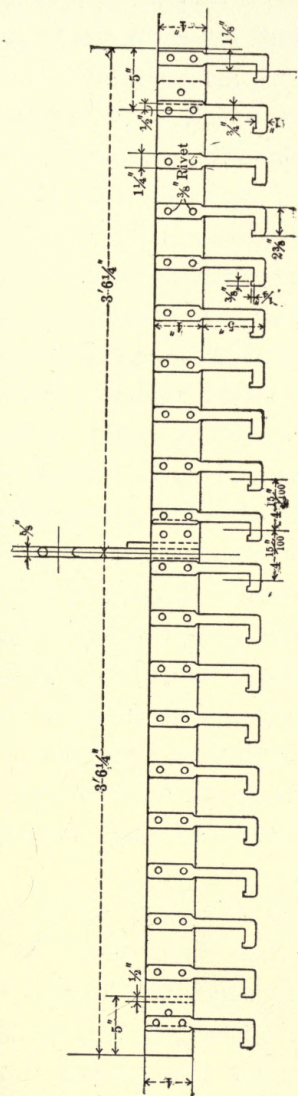
FIG. 55.

bars cool a little more on account of greater surface, increasing their conductivity slightly. Conductors are either placed on top of the tanks or at the side, the best position being on top, as a shorter lug may be used on the electrodes. A bar 1 or  $1\frac{1}{4}$  inches thick and 4 inches wide is suitable. Any necessary bends can be put in by heating the bar to a dull red at the right place, when the bend can be easily put in.

**Cranes.**—The three-motor cranes, though more expensive than one-motor cranes, are to be preferred. Those in use have about a 50-foot span or more and can carry 10 tons nominally. Some cranes have one wire hoisting-rope and one hoisting-drum, and others have a rigid construction with heavy guides at the ends of the electrode racks with a hoist at each end; but they are more expensive, although working faster than the single-rope type. The cranes carry a separate frame with hooks for lifting electrodes, the point of engagement for the anodes being underneath the lug just inside the tank, while the cathodes may be lifted at various places according to the type of cathode.

The set of hooks shown in Fig. 56 has its center of gravity too near the hook to be satisfactory, but it was made this way on account of limited head-room.

The tank-room floor has a fairly large space, about 15 ft. or more in width, at each end for working on electrodes and for the industrial railway. A number of racks for holding fresh anodes properly spaced for the tanks is convenient. These may be brought from the melting-plant best by a crane which commands both melting- and depositing-floors, but also on the industrial railway. A form of rack to economize space is shown in Fig. 57. Before removing the lowest set of anodes, the I-beams for the upper set are lifted out of the way. Three





sets can be stacked as well as two. The cathodes are dumped on flat cars to be taken to the refinery after the supporting bars have been pulled out.

**Floors.**—The floor planking is not nailed down at places near the tanks, to facilitate their removal when cleaning or when repairs are necessary.

**Evaporators.**—Wood tanks and lead pans, with a steam-coil, and also copper pans, have been used for evaporating. None of these are perfectly satisfactory. A copper pan was used at Trail, but copper was dissolved and the refined lead contained copper. It is my opinion, though, that a copper pan can be used successfully by properly protecting it from dissolving. This can be done by having metallic lead in the solution in contact with the pan. Under these circumstances no copper could dissolve until there was a difference of e.m.f. between the lead and any point in the copper pan of about .5 volt. Another method would be to hang a lead pig in the evaporator, connecting the pig as anode and the pan as cathode; by passing a small current the pan could be kept covered wherever wet by the solution with a little lead, and there would be no chance for copper to dissolve on account of the considerable difference of dissolving e.m.f. between lead and copper.

Of course the acid water condensing on the upper part of the pan could dissolve copper, but there would be no trouble in curing this by hanging sheet lead around the sides of the pan.

Wood tanks are not satisfactory for this purpose, while lead pans are, though they do not last long. Their life can be increased by hanging sheet lead over the sides, or by keeping a small current passing with a lead pig as anode, as sug-

gested for the copper pan, so that the tendency is to thicken the pan instead of making it thinner.

A lead steam-coil is satisfactory as a means of heating the solution. The lead dissolves from the coil slowly, but this does not make any serious difference. At Trail, when refining 20 tons per day, one evaporator 20 inches deep, 8 feet wide and 10 feet long, was sufficient to evaporate the wash-water from 2 to 10° B. up to 20° B. It should be noted that the removal of the slime itself reduces the volume of electrolyte in the refining tanks, and as this slime is finally removed wet the volume of the contained wash-water should not be lost sight of in calculating the amount of evaporation necessary. Some evaporation takes place from the lead refining-tanks, which I estimate at about 2.2 cu. ft. per ton refined per day.

The stronger wash-water, if possible, should be added back to the cells without being heated, and only the weaker solutions evaporated to save losses by volatilization. By washing the slime by decantation, and a carefully arranged method of washing, I think it would be possible to get along without any evaporation at all. In fact this was done at Trail at first when the acid loss was as follows:

Aug. 3d—Sept. 16th, 1903, 13.8 lbs.  $\text{SiF}_6$  per ton lead  
 Sept. 16th—Oct. 6th, 1903, 7.7 “  $\text{SiF}_6$  “ “ “

Part of this loss was due to absorption and leakage, and no adequate means for collecting leaks was provided.

Regarding the amount of evaporation from the depositing tanks, I think it very probable that with a well-systematized washing plan, the evaporation from the tanks will take care of all or almost all of the wash-water it is necessary

to use. Just how much evaporation takes place I do not believe has been determined, because of the difficulty in making such a determination in a refinery. We have certain ways of getting at this, however. The voltage between electrodes in the solution being taken at .3, this is a measure of the electric energy expended, which is all absorbed in heating the solution, and this serves to maintain the electrolyte at about 30° C. while the temperature of the room is probably about 17½° C. A large proportion of the cooling of the electrolyte is undoubtedly the result of evaporation. Taking an evaporative efficiency of only 50%, the volume of water driven off per ton lead refined per day would be about 2.2 cu. ft. On the assumption that the cooling air (that is the tank-room air in this case) is saturated with water, and that it escapes from the surface of the liquid three-quarters saturated, Hausbrand's tables\* give for air temperature 15°, and water temperature 30°, 65% of the heat absorbed by evaporation, and 35% by heating, and for 20° and 30°, 60% by evaporation and 40% by heating. My assumption of 50% still allows something for heat loss through the sides of the tanks, especially as the tank-room air is not saturated with water by any means, except occasionally.

This will easily take care of all the water that need be used in washing the slime, and probably of all the wash-water needed altogether.

One cubic foot of ordinary bullion gives about one half cubic foot of wet slime after its removal from the anode.

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\* Hausbrand, "Evaporating, Condensing and Cooling Apparatus," page 327.



TABLE 91.

Plant.	Present Capacity.	Number of Tanks.	Electrolyte Grams per 100 cc.	Electrode Separation.	Current Density, Amperes per Sq.Ft.
1. Consolidated Mining and Smelting Company of Canada, Trail, B. C.	Approximately 80 tons per day	240	6-7 Pb 12-13 SiF <sub>6</sub>	4½ ins.	16
2. United States Metals Refining Company, Grasselli, Indiana.	Approximately 85 tons per day	176	7 Pb 13 + SiF <sub>6</sub>	4½ ins.	12-15 +
3. Newcastle - on - Tyne Plant. Data withheld at request of owners.					

Plant.	Anodes Active Surface.	Average Volts per Tank	Percentage Anode Scrap.	Cathodes.	Anodes per Tank.	Tank Arrangement.
1. Consolidated Mining and Smelting Company of Canada, Trail, B. C.	26×30½ ins. Weight 350 lbs.	.30	15 or less.	2 sets for each set anodes. Weight 150 lbs. each.	20	Cascade.
2. United States Metals Refining Company, Grasselli, Indiana.	2×3 ft. Weight 400 lbs.	.38	25, to be reduced to 15%.	2 sets. Weight 150 to 175 lbs.	28	Walker System.

Plant.	Slime Treatment.	Source of Power.	Size of Tanks Inside.	Generators
1. Consolidated Mining and Smelting Company of Canada, Trail, B. C.	Leaching with sodium sulphide solution. Melting residue to doré after oxidizing sulphides.	Water.	84½×30×44 ins.	1-3500 amperes, 60-110 volts.
2. United States Metals Refining Company, Grasselli, Indiana.	Melting to slag, matte and doré.	Steam.	132×30×43 ins.	1-4500 amperes, 60 volts.

**Power plant.**—The subject of power plants calls for no special remarks here, as more accurate information on that subject that I could give can be got elsewhere. In making estimates of refining cost, the power is usually considered as being supplied separately, and the item for power includes all expenses, interest, and depreciation for the power plant.

**Slime plant.**—All the apparatus mentioned is not applicable to any one process.

**Drying slime.**—This has been done at Trail by filling into wheelbarrows and running them into a warm brick oven and leaving until dry. On dumping the slime into a brick stall it takes fire and roasts itself. It may also be spread on an iron floor, or even in a lead pan gently heated from underneath. Apparatus, as shown in Fig. 58, would be an improve-

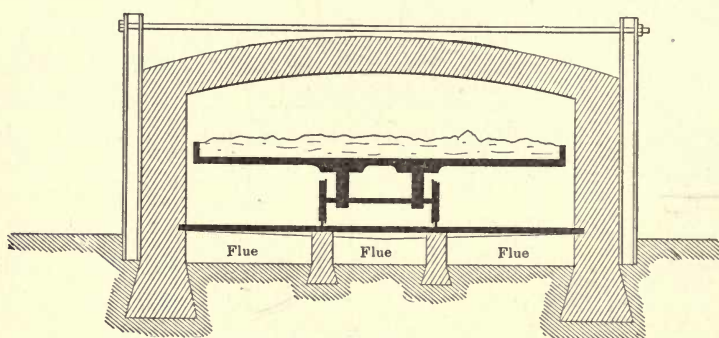


FIG. 58.

ment on the above methods. The heat could be maintained to either dry the slime or roast it, as desired. This apparatus is also applicable to roasting with sulphuric acid.

**Melting slime.**—Magnesia-lined reverberatory furnaces are most used for high temperature work in melting and refining doré. Most varieties of crucibles, including graphite, are rapidly corroded with most slime mixtures. Clay-lined graphite crucibles, I understand, are about the best for the purpose. For melting slime to matte and slag, or metal, matte and slag, iron pots are quite satisfactory, though there is some corrosion of the pot by the slag. Pots arranged as shown in

Fig. 59, while they have not been practically tried, could not very well fail to work, because the metal and matte have very little or no action on iron at the moderate temperatures used.

For melting slime, from which copper, antimony, and arsenic have been removed by wet methods, a silicious slag

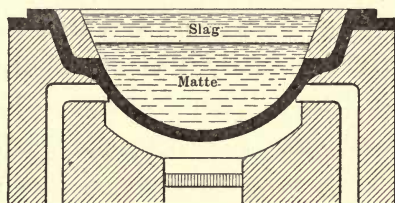


FIG. 59.

should be produced by reacting on the lead sulphate of the slime with silica which is added. This melting can be easily done in crucibles, as no furnace refining is required.

**Leaching slime.**—The treating of slime with ferric sulphate solution, etc., can be done in lead-lined stir-tanks. The solution can be afterward removed by settling and siphoning off the clear liquid. Washing can be done by decantation, or a lead-lined montejus may be used to force the solution into a filter-press. At this period of operation, filter-pressing works well.

Leaching with hydrofluoric acid can be executed in the same tank, if washing by decantation has been resorted to, or in a smaller tank of the same character if filter cakes are being leached. After hydrofluoric acid has been applied in excess, the insoluble residue becomes flocculent and easily suspended, so that agitation by air would be successful here. It is occasionally necessary to add metallic antimony to precipitate dissolved silver, which happens mainly if the slime



has been air-oxidized. Placing chunks of antimony on the bottom of the tank will do, but suspending them with copper wires is more convenient.

Filtration of the antimony fluoride solution is quite simple, but the solution has too much corrosive action on metals, except possibly lead, to permit the use of anything but wood for filters. A gravity filter, with a cloth supported on perforated lead or grooved wood, is successful though slow.

The roasting of leady-copper matte, and leaching it with iron and copper sulphate solution containing free sulphuric acid, is directly analogous to the production of bluestone from matte and sulphuric acid. The most successful methods and apparatus appear to be those described in "The Mineral Industry," Vol. VIII, page 189, and Vol. X, page 231, by O. Hofmann. The pulverizing of the raw matte to 50 mesh is done by a Krupp ball-mill, the roasting in a two-story Pearce furnace; the regrinding is an easier matter, but the method is not described.

The dissolving is done in wood stir-tanks 12 feet in diameter and 6 feet deep, with a 12×12-inch oak paddle for stirring. A truncated cone in the center on the bottom 5 feet 3 inches diameter across the top, and 17 inches high, base 7 feet 6 inches diameter, also of wood, and filled with sand, prevents the matte from piling up in the center of the tank. After reaction is complete, the mixture runs into air-pressure tanks, and is then forced into wood filter-presses, though hard-lead pressures ought to be much better.

The slightly acid solution is neutralized with a little more matte in a deep tank with air-blast for agitation, to remove iron, arsenic, antimony, etc. In the present case, however, the ferrous sulphate present is desired, so sufficient neu-

tralization to remove arsenic, antimony, bismuth, and silica without oxidation, is only needed, with no oxidation.

**Electrolytic antimony depositing tanks.** — Lead-lined wooden tanks well painted are in use and answer well, though a sulphur-treated concrete tank is probably better. The solution should be cooled with a coil of lead pipe, through which water is circulated, connection being made thereto through a long hose to prevent grounding the circuit.

The anodes for depositing antimony consist of soft lead rods about three-eighths inch in diameter, wrapped in two or three thicknesses of muslin. They are merely suspended from copper cross-bars at a distance of three inches apart. These cross-bars can be covered with lead or rubber. In the latter case the rubber is cut away at the places where the lead rod comes in contact with the cross-bar.

The cathodes consist of sheet copper, which have been slightly greased to facilitate the removal of the deposited antimony. The cathodes have a certain small disadvantage, for if they are sufficiently greased to permit the easy removal of the antimony, the antimony is likely to drop off to some extent in the tanks, as it curls away from the cathodes, and if they are not greased enough the cathodes have to be bent and wrinkled to get all the antimony off. It is, however, not necessary to get all the antimony off each time, and if pieces fall in the tanks they can be readily collected. A current density of 15 amperes per square foot, volts about 2.9 to 3.0, and a distance from center to center of cathodes of about 4 inches may be recommended, though this can perhaps be improved upon.

Wrapping the anodes should be done with muslin strips put on diagonally, with a string or elastic band around each

end to hold it. The anodes should not be allowed to dry with acid on, as this rots the cloth; nor should the solutions be too strong or contain too much sulphuric acid, for the same reason. The best way to do is to keep the anodes in use as continuously as possible, and if the tank has to be shut down, fill it with water. The anode scrap can be thrown into the lead-furnace of course, cloth and all. The production of antimony is small, so that individual handling of electrodes with a block attached to an overhead trolley parallel to the long side of the tanks is all that is necessary. The form of tank is shown in Fig. 60.

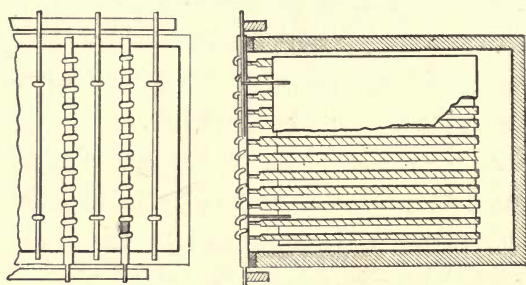


FIG. 60.

**Electrolytic ferric sulphate tanks.**—The chemical and electrochemical side of ferric-sulphate production has been treated elsewhere. In constructing the electrolytic tanks, the following diaphragms are available and practical: Perforated lead sheets in pairs with asbestos paper or asbestos board between; perforated wooden boards with the holes closed with asbestos, and hardened asbestos mill-board. All may be used interchangeably as diaphragm plates. From the electrical standpoint, the lead diaphragm is the best, on account of the low resistance of these diaphragms consequent



on the large relative area of the holes, while the hardened asbestos board has the greatest resistance. The resistances have not been accurately measured, but Table 92 (page 262), from tanks of various sizes in operation, is of interest.

Of the above tanks all but No. 2 gave high current efficiency; No. 2 had internal leaks and gave a low efficiency.

Fig. 61 illustrates a tank for 3500 amperes. The cathode bus bar runs lengthwise in the center of the tank, and a cath-

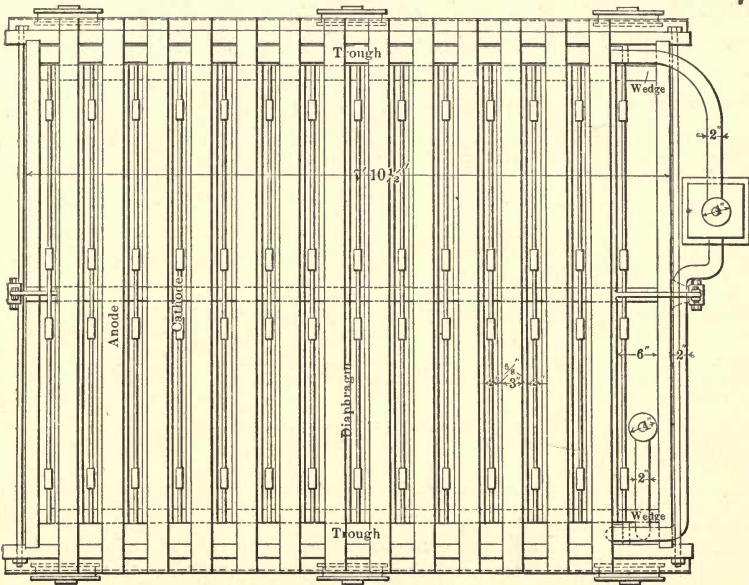


FIG. 61.

ode is placed on each side in each compartment. The anodes are of Acheson graphite one inch in diameter, spaced  $1\frac{1}{2}$  inches centers. The anodes are inserted in the channel irons, and cast in lead, which makes a good contact. The sheet-copper cathodes, cross bars, and lead lining of the tank call for no special remark. The circulation of the anolyte, which is quite

TABLE 92.

Diaphragm.	Date.	Electrode Separation.	Diaphragm.	Holes.	Holes Center to Center.
1. Wood and Asbestos.	Sept. 1903	3" centers.	$\frac{1}{8}$ " wood, bored, and holes filled with asbestos.	$\frac{1}{2}$ "	
2. Wood and Asbestos.	1905-1906	3 $\frac{1}{2}$ " centers.	$\frac{3}{4}$ " wood, bored, and holes filled with asbestos.	$\frac{3}{4}$ "	1 $\frac{1}{2}$ "
3. Lead and Asbestos.	June, 1906	4 $\frac{1}{2}$	2 $\frac{1}{2}$ lb. lead sheets, asbestos paper between.	$\frac{3}{8}$ "	$\frac{3}{4}$ " average.
4. Sulphurized Asbestos.	1906	3 $\frac{1}{4}$	$\frac{1}{4}$ " asbestos, with absorbed sulphur.		
5. Sulphurized Asbestos.	1906	3 $\frac{1}{4}$	$\frac{1}{4}$ " asbestos, with absorbed sulphur.		

Diaphragm.	Date.	Compartments.	No Compartment.	Active Cathode Area.	Solution.	Temperature.
1. Wood and Asbestos.	Sept. 1903.	18" $\times$ 13" $\times$ 3"	11	13.8 sq. ft.	3% $\text{H}_2\text{SO}_4$ 4% $\text{Fe}'' + \text{Fe}''$ 3% $\text{Cu}''$ " "	28° C. 40° C. 41° C.
Wood and Asbestos.	1905-1906.	33" $\times$ 5 ft.	23	260 sq. ft.	3.4% $\text{H}_2\text{SO}_4$ 4% $\text{Fe}''$ 3% $\text{Cu}$	40° C. 50° C.
3. Lead and Asbestos.	June, 1906.	3 $\frac{1}{4}$ " $\times$ 29 $\frac{1}{2}$ " $\times$ 12 $\frac{1}{2}$ "	3	3.33 sq. ft.	5.5% $\text{H}_2\text{SO}_4$ 3.5% $\text{Fe}$ 3.75% $\text{Cu}$	62° C.
4. Sulphurized Asbestos.	1906.	33" $\times$ 23"	7	24 sq. ft.	4-5% $\text{H}_2\text{SO}_4$ 4% $\text{Fe}$ 3% $\text{Cu}$	40-50° C.
5. Sulphurized Asbestos.	1906.	33" $\times$ 23"	7	24 sq. ft.	4-5% $\text{Fe}''$	44° C.

Diaphragm.	Date.	Amperes.	Volts.	Amperes Sq. ft.	Kind of Carbon.	Notes.
1. Wood and Asbestos.	Sept. 1903.	115 100 90	2.25 1.60 1.50	8 3 7.25 6.5	Amorphous Carbon.	Polarized stationary anodes. Clean anodes, moving, no polarization.
2. Wood and Asbestos.	1905-1906	2000	2.0	7.7	Graphite.	No polarization. Internal leaks. Poor efficiency.
3. Lead and Asbestos.	June, 1906.	8. 33.	1. 1.7	10.0	Graphite.	Normal conditions of current and voltage.
4. Sulphurized Asbestos.	1906.	200-240	2.4?	8.3-10	Graphite.	Copper-slime treatment.
5. Sulphurized Asbestos.	1906.	140	1.6	5-8	Graphite.	Lead-slime treatment. Silica in solution and anodes afterward polarized.

vigorous between the various anode compartments, and of the catholyte which circulates freely around all cathodes, is maintained by two separate air-lifts, one for catholyte and one for anolyte. The diagrams, Fig. 62, will explain the circulation.

The tank is operated continuously, and the anolyte and catholyte do not change in composition, the maintenance at a practically constant composition being assured by the continual inflow of fresh solution.

The inflowing solution contains about 3% of copper and 5% of ferrous iron, beside 2 to 5% of sulphuric acid. The

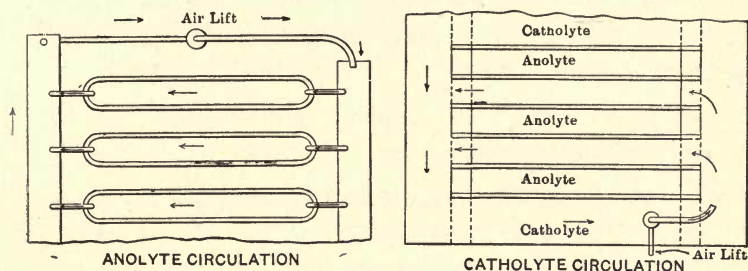


FIG. 62.

catholyte contains about  $\frac{3}{4}\%$  of copper and the same amount of ferrous iron and acid.

The level of the catholyte is higher than the anolyte by a half inch or so, depending on the diaphragm, and the result of constant feed of fresh solution is that catholyte continuously flows in a small stream or percolates to the anolyte, which assays about the same in free acid and copper as the catholyte, but contains only 0.8–1.0% of ferrous iron, the rest being ferric iron. The result of continuous feed is of course continuous overflow of finished ferric sulphate solution, through a run-off pipe provided therefor.



In putting the tank together, the main point is not to have any internal leaks from catholyte to anolyte and vice versa. There is no difficulty about this if the following method

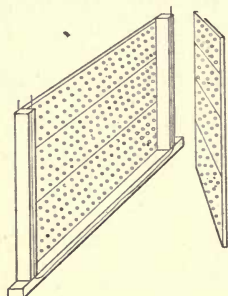


FIG. 63.

is adopted. In the first place the diaphragms, if of wood, are of separate boards, which should be tongued and grooved. These boards fit between two frames, one on each side. A small piece of round asbestos packing should be tacked on the distance frames, with small brads, before placing the diaphragms. When the whole is driven together by the end wedges, this makes a good

joint. See Fig. 63.

The lift required to circulate the solution is only about 3 inches at most, and the height can be easily got with a 3-foot depth of solution in the air and solution pipe.

The siphons for feeding anolyte to and from the various compartments are rather hard to manage and keep working unless provided with a small pipes at the top for drawing air out, as in Fig. 64. The anode connection may be made by a copper bar lying on the center of the anode frame, directly over the cathode bus bar, with large wires attached over each channel-iron and with the other end buried in the lead. A flexible connection is required of course from the anode bus bar to the outside source of current.

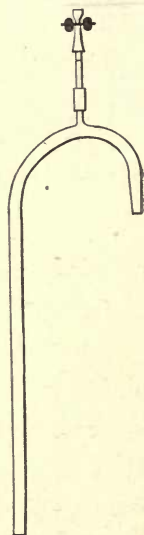


FIG. 64.

The anolyte is a little heavier than the catholyte, and by

supplying the necessary heat to the anolyte, this may be corrected a little by its greater heat expansion, thus diminishing the tendency for mixing, existing especially in deep tanks.

A lead pipe, heated by steam, lying in one of the anolyte troughs at the side of the tank does the heating well. A piece of  $1\frac{1}{2}$  pipe, 6 ft. long, is enough for a large tank.

Fig. 65 shows a smaller tank for 250 amperes. The hardened asbestos diaphragms are 38 by 25 inches. By increasing these to 40 by 40 inches, and putting more compartments into the tank, it could be easily extended to take 2000 or 3000 amperes. The diaphragms are made as follows: Powdered sulphur is sifted evenly over the surface of  $\frac{1}{4}$ -inch asbestos mill-board in the amount required, namely, about  $\frac{1}{4}$  lb. of sulphur per square foot for a sheet of this thickness. The sheet is then slid into an oven heated by an oil bath to a temperature of 120–140° C. for one or two hours, or until all the sulphur has melted and soaked in. The sheet is taken out, cooled, and an equal amount of sulphur put on the other side and heated again. The board is cooled on a perfectly flat floor, and makes a hard, slightly elastic and waterproof product.

Before putting the diaphragms into the electrolytic tanks, they ought to be soaked about two weeks in very dilute sulphuric acid, as some expansion takes place at first. Otherwise the sheet will warp in the tank. The method of assembling and packing the joints is the same as for the tank just described. This construction and diaphragm gives a tank which is so tight internally that it allows no mixing of anolyte and catholyte, even if there is a considerable difference in level between the two, and it is necessary to use a small siphon to keep catholyte always flowing to the anolyte.

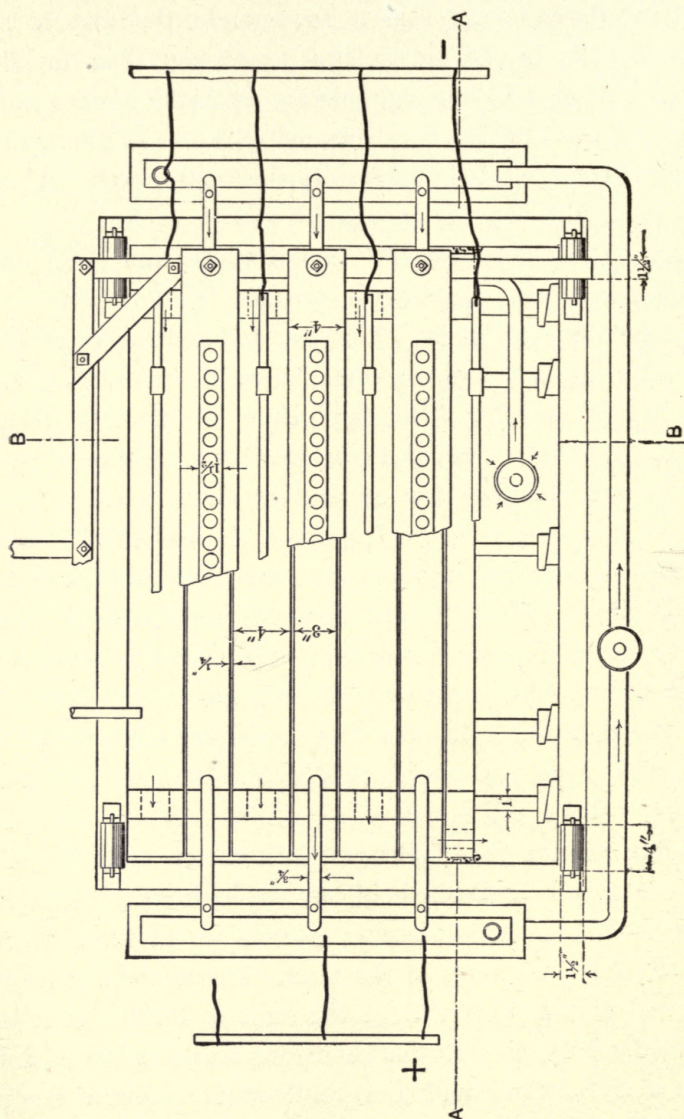


FIG. 65.

Storage capacity should be provided at a higher level to hold sufficient solution to feed the tanks for 36 to 48 hours,



and at a lower level to receive the overflow for the same time. The iron in the solution should not be less than 5% and could very likely be 6 or 7%, though this has not been attempted yet. The ferrous iron in the overflow should be 0.8 to 1.0%, the remainder being ferric iron. With 50 gr. total iron per litre 1000 amperes produces about 45 cubic feet per day per tank containing 10 gr. ferrous iron per 1000 cc.

Electrolytic tanks, depositing copper from sulphate solution with insoluble lead anodes and no diaphragm, are too simple to call for much remark. In the execution of the ferric sulphate process, after neutralizing with matte, electrolysis of the solution with a lead anode, until a few per cent of free sulphuric acid is present, could be practiced, and would be more economical unless sulphuric acid was very cheap.

**Refinery operation and costs.**—The tank-room operations can be arranged so that little labor is required on Sunday or at night. The daily operation includes charging and emptying a certain number of tanks and drawing cathodes and replacing them in an equal number of other tanks, the practice being to make two sets of cathodes from each set of anodes. The operation of changing cathodes is simple, but requires care to keep the old cathodes from wiping slime from the anodes as they are pulled out, and the new cathodes on account of their usual flimsy character have to be handled delicately. In view of the greater ease of handling and superior electrical and chemical results, I believe a steel cathode, as described on page 228, with wooden strips 1 inch square having a groove on one side, slipped over the edges, ought to be used, though they are not now. These strips may be seen in the photograph, Plate 7.

Grooves around the plates will take the place of wood strips.\*

It is necessary to inspect the tanks with a voltmeter to detect short circuits, and any short-circuited plates are taken out and straightened.

At Trail, B. C., after removing the cathodes, the anodes are taken out, a tank-load at a time, and the anode slime is removed in separate tanks, by wiping the scrap with rubbers and pouring water on afterward to clean off the muddy solution. Another way is to hang the whole tank-load in a special tank to receive the slime, and reach down between the plates with wipers to loosen the slime, after which a spray is turned on the plates. This is quite readily done, but apparatus shown in Fig. 54, is believed to be better yet, although not yet in use. This apparatus will clean a whole tank-load at once, after which they may be sprayed with a set of spray-pipes.

After the anodes have been taken from the tank, the circulation of electrolyte is shut off, by connecting the overflow of the tank next above and the feed of the one next below with a hose. The clean solution is then siphoned from the tank into a launder beneath the tanks which carries the solution to the storage tank. The workman, with rubber boots on, next gets into the tank and shovels the slime into a barrel. This is more troublesome and less satisfactory than sluicing the slime into a car beneath the tank, because the tank should be absolutely clean when solution is next admitted. Otherwise the remaining slime is stirred up, which is a bad thing for the cathodes. It should be remarked, however, that it is not necessary to clean out a tank at the end of each run as a gen-

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\* U. S. Patent, Elliott and Kishner, 683283. October 12, 1901.



eral thing, for most or all the slime comes out on the anode scrap, unless the anode bullion is unusually pure. Usually the anode hardly changes its appearance during the whole depositing operation. To fill the cleaned tank, it is only necessary to run a hose to it from the high-level storage tank and start the solution by opening a valve or by siphoning. The temporary hose to carry the circulating solution around that tank is then disconnected and taken away.

The cathodes are best washed by spraying with warm or hot water, though they have also been washed by dipping into a tank containing wash-water. If the wash-water is used over and over, until it reaches the strength of the tank solution, there is a loss of solution of course, as it will not all drain off. The amount of solution that it takes to wet the cathodes varies of course with the cathode thickness and roughness. With the samples shown in Plates 2 and 3, pages 38 and 39, the amount required to wet them, and corresponding acid loss, with the weight of cathodes per square foot, is given in Table 93.

TABLE 93.

No. in Photograph.	Weight per Square Foot.	Solution on Cathode.	Acid Loss per Ton Lead.	Actual Loss.	Remark.
2	28.8 lbs.	.5 %	1.66 lbs. $\text{SiF}_6$	.83 lbs. $\text{SiF}_6$	Average cathode.
4	22 "	.39%	1.33 " $\text{SiF}_6$	.67 " $\text{SiF}_6$	Average cathode.
5	16 "	.36%	1.2 " $\text{SiF}_6$	.60 " $\text{SiF}_6$	Unusual cathode.
6	1.1 "	.22%	.76 " $\text{SiF}_6$	.38 " $\text{SiF}_6$	Unusual cathode. Not well wetted.

The actual loss, if the cathodes are first washed with wash-water, and this is used over and over until the same strength as electrolyte, would be one-half the loss if the cathodes are



merely drained. At  $7\frac{1}{2}$  cents per pound of  $\text{SiF}_6$  the maximum saving is so small, that a more systematic method of washing would not be apt to pay. The amount of wash-water to be returned to the tank by this method equals the amount taken out on the cathodes, so no evaporation is required.

The surface of the anode scrap is only from one-third to one-half that of the two crops of cathodes for each anode, and the anode scrap is smoother too, so that the acid loss from solution and wash-water required to wet anode scrap, is about 30 to 40% of that on the cathodes.

The acid loss in fairly well-washed slime depends somewhat on the amount of slime. For an average grade of bullion containing 96-97% of impurity, the loss in fairly washed slime will not exceed 2 lbs.  $\text{SiF}_6$  per ton of lead, so that the total losses on and in material removed will not exceed about 3.1 lbs., if it is that high. When it comes to evaporation, which is, however, not absolutely necessary, there is a chance of boiling off acid.

The anode scrap and cathodes are usually carried by the crane directly to the melting-pots and dumped in, the cathode cross-bars of course being first pulled out.

For disconnecting tanks from the electric circuit while cleaning them, a small copper block and a clamp is all that is necessary. For disconnecting one tank it is usual to place copper rods across from side to side, resting on the conductors on each side of the tank. Sometimes the cathode supporting-bars can be used, but usually they are too short to reach, and a few bars of special length are necessary.

The tank inspector has a voltmeter supported by straps around the neck and shoulders so that it lies open in front of him. The leads are connected to a pair of small ice-picks.

With one in each hand, the voltage of all the cathodes in a tank can be quickly read. Any short circuits may be indicated by chalk marks, to be fixed by moving the electrodes slightly, or if necessary, by taking the cathodes out and straightening them.

Slime is variously washed by decantation, and by filter-pressing. The results obtained by washing by decantation, are mentioned on page 247. In washing anode slime by decantation, if hot wash-water is used, the slime breaks up better and is more rapidly mixed with the wash-water.

Elevating slime either to washing-tanks, or to a filter-press, should not be attempted by a monteju, this having been a partial failure several times. It ought to be mechanically elevated in tanks, or driven through a good-sized iron pipe with a pump. The former of these two methods was in use at Trail at first, and is sure, though clumsy.

The various wash-waters from cathodes and anode scrap should be filtered and run to a storage tank, and then evaporated if necessary. The strong wash-water from the slime can go directly to the electrolyte storage tanks.

Making cathodes, as invented by Dr Wm. Valentine (see page 231), requires one man, who makes and hangs at least 10 sheets an hour. One man can make 400 sheets of the kind used at Trail, or enough for 30 tons of lead, in a day, and in eight hours two men can hang and straighten the same number of sheets, so that the cost for sheets, with labor at \$2.00, is about 20 cents per ton. The cost for Valentine cathodes is then a little higher, but they have certain advantages over the old style, in giving better and more uniform contacts, and the lugs being made thicker than the plate itself, reduces very much the liability of the cathodes being cut

through by the electrolyte at the surface, and dropping in the tanks. To prevent this with the old style of cathodes, a streak of asphaltum paint was put on where the surface of the solution comes. There is no doubt but what the molds for making Valentine cathodes can be improved so as to save considerable labor.

The labor cost for operating tanks, that is, charging and drawing and washing and cleaning electrodes, cleaning tanks (on the supposition that the slime is sluiced out into a car underneath), inspecting tanks and fixing short circuits, handling anode scrap and weighing, may be taken in detail as follows, for a production of 100 tons lead per day:

TABLE 94.

Charging tanks. ....	4 men	8 cents per ton.
Emptying tanks. ....	4 "	8 " " "
Cleaning tanks. ....	4 "	8 " " "
Inspecting tanks. ....	9 " , 3 shifts,	18 " " "
Weighing and tramming. ....	3 "	6 " " "
Cleaning and handling scrap. ....	4 "	8 " " "
Repairs. ....	2 "	6 " " "
Making and straightening sheets. ....	10 "	20 " " "
Other operations. ....	2 "	4 " " "
<hr/>		
Total tank-room labor. ....	42 men	86 cents per ton.

By the use of steel cathodes I believe this cost can be reduced to about 60 cents per ton, by removing the necessity of making starting sheets and of much inspecting, beside improving results.

The labor cost of loading pig lead and unloading bullion, sampling, weighing and tramming to and from melting plant, would be about 19 cents per ton refined.

In the melting plant, about 100 lbs. of coal or less is used per ton of lead refined. The labor cost charging the kettles



and molding anodes and lead and stacking the anodes, is about as follows:

TABLE 95.

Charging furnaces with lead, and skimming.....	10	cents	per	ton	refined.
Molding lead, including firing. ....	9	"	"	"	"
Molding anodes and stacking, including firing.....	13	"	"	"	"
Repairs, including new pots.....	6	"	"	"	"
Coal. ....	10	"	"	"	"

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48 cents per ton refined.

It might be of interest to state the approximate labor cost when handling electrodes singly with an overhead trolley, hoisting being done by a chain block, on a scale of 10 tons per day.

TABLE 96.

Unloading anodes from cars. ....	6	cents	per	ton	refined.
Tramming to tank-room.....	4	"	"	"	"
Straightening and charging anodes.....	30	"	"	"	"
Making starting sheets. ....	25	"	"	"	"
Inspecting and night man. ....	45	"	"	"	"
Charging cathodes. ....	8	"	"	"	"
Drawing and washing cathodes. ....	12	"	"	"	"
Drawing and cleaning anode scrap.....	40	"	"	"	"
Molding. ....	25	"	"	"	"
Loading on cars. ....	10	"	"	"	"
Unclassified.....	40	"	"	"	"

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Total tank-room labor cost. .... \$2.45 cents per ton refined.

The anodes are supposed to come to the refinery already cast, and merely need straightening. The figures are per ton refined lead produced, assuming a wage of 20 cents an hour. The labor could be reduced considerably.

### Comparative Costs of Refining by the Parkes and Betts Processes.

*Parkes Process.*—Assuming that all approved labor-saving machinery is used, that the bullion contains .7% Sb, .8% Cu, and 75 ozs. silver with a little gold, coal at \$2.50 and coke at \$5.00, zinc at 6 cents, and a production of 100 tons per day average wages \$2.00 per day:

TABLE 97.

400 lbs. coal per ton bullion received at works. . . . .	\$0.50
65 lbs. coke for reducing hard lead, retorting, etc. . . . .	0.16
Zinc, 16 lbs. . . . .	0.96
Repairs and supplies. . . . .	0.25
Parting and refining silver and gold. . . . .	0.19
Fluxes. . . . .	0.11
Labor, softening and desilverizing. . . . .	0.23
Labor, retorting. . . . .	0.07
Labor, cupelling. . . . .	0.05
Labor, power plant. . . . .	0.14
Labor, working by-products. . . . .	0.34
Foremen and general labor. . . . .	0.40
Mechanics and helpers. . . . .	0.18
	<u>\$1.41</u>
Labor, except parting plant. . . . .	\$1.41
Refining charge on 12 lbs. copper. . . . .	0.09
	<u>\$3.67</u>

No published detailed costs of refining as it is done at present, exist as far as I know. The above are compiled from various sources of published and private information.\*

The above assumptions may be criticised on the ground of too high a percentage of copper in the bullion. With .2-.3% of copper, the costs would be about 15 cents less.

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\* I am much indebted to Mr. Ernst F. Eurich for figures which have been largely used in compiling the above statement.

*Betts Process* costs on same bullion, with the same assumed cost of coal and labor:

TABLE 98.

Power 7.6 H.P. days total at \$50 per E.H.P. year. ....	\$1.06
Tank-room, platform, and repair labor. ....	0.86
Melting lead, labor, supplies, repairs. ....	0.38
Coal for melting lead. ....	0.13
Chemicals, 6 lbs. $\text{SiF}_6$ , at 6 cents .....	\$0.36
$\frac{3}{4}$ " glue. ....	.07
Slime treatment, except power and assaying, including parting....	0.96
	<hr/>
	\$3.82
Credit about 20 lbs. electrolytic copper recovered from matte at 3 cents	.60
	<hr/>
Net cost. ....	\$3.22

For a complete comparison of the two processes it is necessary to take into account the metal losses, interest on plant, and general expenses. The lead loss in the electrolytic process is practically none, as even the lead in the slime is returned to the lead blast-furnace. Five pounds lead per ton is an outside estimate of loss. The zinc process will lose about 1% of the actual lead present. The antimony loss is respectively 10% or less and 40%, while the electrolytic antimony from the electrolytic process is also usually more valuable than antimony in hard lead. The silver loss should be calculated on actual contents, which is  $1\frac{3}{4}\%$  greater (about) than that shown by commercial fire-assay. There is no opportunity for appreciable silver loss in the electrolytic process, while with the zinc process the loss ascertained from various sources of information may be taken at 1% as an average for good work. The same figure can be certainly surpassed by the electrolytic process, but lacking clean-up figures from lead refineries, I assume the same figure for silver loss for the electrolytic process as for the zinc process.



TABLE 99.

	Parkes Process.	Betts Process.
Net working cost.....	\$3.67	\$3.22
Interest on plant at 10%*.....	.55	.55
Lead loss, at 5 cents per lb. ....	1.00	.25
Antimony loss, at 15 cents per lb. ....	.84	.21
Interest on metal in process, at \$150 per ton, at 6%.....	.10	.24
Interest on by-products and doré.....	.07	.07
Superintendence and assaying.....	.15	.15
Silver loss, actual.....	.50	.50
	\$6.88	\$5.19

\* Interest on power plant not included, as this is figured as part of power cost.

Other items for expressage, management, taxes, insurance, etc., I assume to be practically the same for each process. The above estimate applies to the purer grades of bullion, free from bismuth. Copper does not average as high as .8% in many cases, but that is usually the result of skimming the bullion at the smelter, the dross going back to the lead furnaces and yielding copper-lead matte; but the end-result is the same whether the copper dross is skimmed by the smelter or refiner, for the metallurgical process is the same in each case.

If bullion with more impurity is under consideration, the relative advantage of the electrolytic process is greater. For example, if the bullion contains say .05% of bismuth, not a large or unusual amount, the electrolytic process produces corroding lead, while the zinc process does not, making a further difference in this country, apart from the value of the bismuth saved, of \$2.00 to \$2.50 per ton. With higher antimony the advantage of the electrolytic process again increases,

the amount being easily figured from the known difference in antimony loss, 10% and 40%, and the value of pure lead and antimony, as against that of the same combined in hard lead.

The present aim of lead smelters is to exclude from the furnaces ores containing antimony and especially bismuth in order to produce as pure bullion as possible. If the lead is refined electrolytically, these metals become a source of profit, and the way is opened for the utilization of low-grade bismuth ores particularly.

The following table shows the cost of the two processes under the head of labor, coal, chemicals and zinc.

TABLE 100.

	Parkes Process.	Betts Process.	
		Steam Power.	Gas Power.
Labor.....	\$1.41	\$1.89	\$1.89
Fuel for all purposes at \$2.50. . .	0.75	0.58	0.35
Chemicals. . . . .	0.05	0.66	0.66
Zinc. . . . .	0.96		

This shows labor to be less with the Parkes process, while fuel and materials are less for the electrolytic process. I have assumed that the coal is of good quality and 2 lbs. are required to generate 1 E.H.P. hour with steam, and 1 lb. with gas engines. The fuel for the Parkes process includes the fuel for treating by-products up to and including fuel used in refining copper.

The following estimates of cost of a refinery to treat 50 tons of bullion per day, with a maximum capacity of 60 tons,

will serve as a basis for other calculations under special conditions.

The cost of construction is greatly different with different arrangements of plant, cascade system, Walker system or series system, and slime plant. The following figures apply to the Walker system. The most economical arrangement of tank plant and melting plant I believe to be is to have the two parts under the same roof, in a long building and commanded by the same cranes. The anodes can then be taken directly from the casting floor to the tanks without rehandling, and the cathodes, after spraying, can be dumped directly from the tanks, in or near the melting furnace, depending on the kind of furnace. To save in the number of trips required of the crane, which would have to be operated steadily to load and unload as much metal as 60 tons per day from melting floor to tanks and back, the tanks would be made of the largest practicable size, to take 6500 amperes, for 60 tons production. There would be two cranes on the single runway, in a building  $55 \times 250$  feet, of which 100 feet in length would be occupied by the tanks. The melting room need not necessarily be limited to the same width as the tank floor.

The cathodes are assumed to be of lead-plated steel, which will save enough in a year in operating cost to pay for themselves. The current density to be 15 amperes per square foot for 50 tons per day, and 18 amperes for 60 tons per day. The current efficiency is assumed to be 90%, and will probably average 95% with steel cathodes.

The power plant would be required to deliver a maximum of 6500 amperes and 43 volts (=280 K.W.) to the depositing tanks. If only 50 tons per day were produced 197 K.W. are required, and for 40 tons per day 128 K.W. The power plant,



if in a single unit, should be capable of operating efficiently from less than half its maximum capacity, all the way up. The power for treating slime and general power and lighting will be included in the estimate later.

Power plant for lead depositing at \$135 per K.W. ....	\$38,000
104 depositing tanks 3 feet wide, 3 feet 10 inches deep, 8 feet 6 inches long inside. ....	5,200

200 feet $\frac{1}{2}$ steel rods. ....	\$4.00
Labor on concrete. ....	10.00
Molds expenses. ....	2.00
3 barrels cement. ....	4.50
22 cubic feet sand. ....	1.00
43 cubic feet rock. ....	2.40
375 lbs. sulphur. ....	4.70
Fuel. ....	.50
Paint. ....	1.00
Concrete piers and beams. ....	12.00
Labor coating tanks. ....	3.00

---

\$45.10

Wood tanks are more expensive.

Lumber, 650 ft. yellow pine at \$35.00. ....	\$27.50
Labor, 50 hours. ....	15.00
Iron, 200 lbs. ....	8.00
Paint. ....	1.50
Piers and timber supports. ....	10.00

---

\$62.00

Electrolyte, about 7000 cubic feet. ....	7,000
--	-------

70 tons fluorspar at \$14.50. ....	\$980
80 tons sulphuric acid at \$15. ....	1,200
18 tons fine quartz at \$20. ....	360
20 tons white lead at \$120. ....	2,400
Labor. ....	1,250
Repairs. ....	500
Coal. ....	200

---

\$6,890

For grading and preparing solution-tight floor under tanks, on a level site, about.....	1,000
Tank part of building 55×140 ft. at \$1.25 per square foot for walls and roof.....	9,600
2 electric cranes installed.....	12,000
Copper for bus bars at 25 cents per lb. ....	1,250
Concrete electrolytic storage tanks. ....	500
2400 steel cathodes $\frac{1}{8}$ " thick at 3 cents. ....	5,400
Labor and material for same. ....	1,200
Pumps, hose, cleaning tanks, electrode racks, starting-sheet apparatus, evaporator, slime-washing tanks, lights, water connections, tracks, cars, sulphur tank, total. ....	5,000
Royalty for use of Walker system. ....	
Hydrofluoric-acid plant. This is quite cheap to instal, and may be expected to cost \$1,500 or less for a good-sized plant. ....	1,500
Total for tank plant, exclusive of royalty. ....	\$49,650

The cascade arrangement would cost more, about as follows:

For more building.....	\$3,000
For more copper at 25 cents.....	2,275
For power plant to supply power lost in conductors. ....	1,690
	<hr/>
	\$6,965

Melting plant costs:

3 60-ton kettles complete with stack.....	3,110
Cast iron, at 3 cents. ....	\$1,300
55,000 red brick, at \$10.....	550
12,000 fire-brick, at \$30.....	360
Mason's labor. ....	700
Supplies. ....	100
Reinforcing iron. ....	100
	<hr/>
	\$3,110
Building, about 6,000 sq. ft.....	8,000
Molds, open. ....	275
Tracks, cars and hoists, crane runway, etc.....	3,000
	<hr/>
	\$14,385

Slime plant, to treat daily 600 lbs. copper, 1,200 lbs. antimony, 400 lbs. arsenic, 3,750 ozs. silver and gold, and 250 lbs. lead, in slime, beside 2 tons of copper-lead matte:

Slime-dissolving tanks for ferric solution, total capacity 1,000 cu. ft.	1,200
Antimony-dissolving tanks, 150 cu ft. ....	300
Lead filter-press, with montejus, for slime. ....	600
Storage tanks, lead-lined, for sulphate and fluoride solutions, 3,500 cu. ft. capacity. ....	1,500
18 2,000-amp. copper-iron electrolytic tanks. ....	6,300
10 2,000-amp. antimony tanks with cathodes. ....	1,250
Crucible melting furnaces for antimony, gold, silver, doré, with molds. ....	1,000
Parting plant. ....	600
Building, about 5,000 sq. ft., at \$1.50 per sq. ft. ....	7,500
Dissolving tank for matte ....	600
Filter press and montejus for matte. ....	600
Roasting furnace. ....	1,000
Accessory apparatus. ....	2,000
Filters for antimony solution. ....	100
Mill for grinding matte. ....	500
	<hr/>
	\$25,050

Power plant for treating slime, capacity 120 K.W., at \$135..	16,200
For general purposes, 30 H.P., at \$135. ....	4,050

Total costs of refinery, maximum capacity 60 tons per day, would then be:

Power plant. ....	\$58,200
Tank plant. ....	49,150
Melting plant. ....	14,385
Slime plant. ....	25,050
	<hr/>
	\$146,785

Engineering expenses, railroad facilities, land, contingencies not included.

A series plant for a maximum production of 60 tons per day, provided with a plant to treat slime by the roasting-with-sulphuric-acid process, would work out about as follows:

Maximum current density 16 amperes per square foot. Thickness of electrodes to be  $\frac{1}{2}$  inch, and spaced  $1\frac{1}{4}$  inches apart.



Volts per plate .22, efficiency 90%. Anodes 3 feet square. Tanks  $4\frac{1}{2}$  feet deep, 3 feet 2 inches wide, and 8 feet 4 inches long, taking 56 plates and producing with 144 amperes, 1,450 lbs. of lead per day, or refining about 1,490 lbs. of bullion. 88 tanks arranged in 11 sets of 8 tanks each, 10 sets always in use, absorbing altogether 1,440 amperes and 100 volts.

Lead-depositing power plant 145 K.W., at \$135.....	\$19,600
88 tanks of concrete, at \$55.....	\$4,840
Electrolyte, about 8,000 cu. ft.....	8,000
2 electric cranes.....	12,000
Copper conductors, 2,500 lbs.....	625
Preparing floor under tanks.....	1,000
Building, 55-125 feet at \$1.25 per sq. ft.....	8,500
Hydrofluoric-acid plant.....	1,500
Electrolyte storage tanks.....	500
Accessories.....	5,000
<hr/>	
Tank room and equipment.....	\$41,965
Melting plant, using rolls to roll anodes or closed molds.....	\$22,000
Slime plant, using roasting with sulphuric-acid process:	
Mixer for slime and $H_2SO_4$ .....	\$250
Flat cars and oven for drying slime.....	2,700
Electrolytic copper tanks, 15 for 700 amp.....	800
Electrolytic antimony tanks, 23 for 700 amp.....	1,500
Dissolving tanks, with stirring-gear.....	800
Filter press and montejus.....	600
Storage tanks.....	1,200
Evaporators for $H_2SO_4$ .....	200
Crucible melting furnaces.....	1,000
Parting plant.....	600
Building about 3,000 sq. ft., at \$1.50.....	4,500
Accessories.....	2,000
<hr/>	
Total.....	\$16,150
Power for slime treatment, 75 K.W.	
“ and lights, 30 K.W.	
105 K.W. at \$135.....	\$14,200

For a comparison between the two methods of installation we have for plants with 60 tons maximum capacity:

TABLE 101.

Power plants. . . . .	\$ 58,200	\$ 33,800
Tank plants. . . . .	49,150	41,965
Melting plants . . . . .	14,385	22,000
Slime plants. . . . .	24,050	16,150
	<hr/>	<hr/>
	\$145,785	\$113,915

Allowing for land, engineering expenses, shipping facilities, etc., total cost may be taken at \$2,000 to \$3,000 per daily ton capacity. The above figures are only intended to serve as a basis for computations, and not to furnish exact information, which it is impossible to do anyway as costs are subject to great variations, so in many cases I have not thought it worth while to try to ascertain exact costs of different apparatus.



## CHAPTER VIII.

### PRODUCTS.

THE analyses of refined lead, presented as tables, are collected from numerous sources, and are not selected in any way, but include all the analyses I have. The Consolidated Mining and Smelting Company of Canada, Ltd., have kindly given me the *average* analyses of their electrolytic lead and lead bullion, which is given as Table 102.

TABLE 102.

#### BULLION.

	Au	Ag	Cu	Fe	Sb
1904 averages. ....	1.50 ozs.	200 ozs.	.50%	.07%	.55%
1905 " .....	1.00 "	109.1 "	.19%	.05%	.44%
1906 " .....	.....	.....	.20%	.....	.81%
1907 " so far. ....	.....	.....	.20%	.....	.75%

	Sn	As	Mn	Zn	Bi
1904 averages. ....	Trace	.11%	Trace	Trace	None
1905 " .....	"	.23%	"	"	"
1906 " .....	None	.15%	"	"	"
1907 " so far. ....	Trace	.25%			

TABLE 103.

#### PIG LEAD.

	Silver	Cu	Fe	Sb	Sn	Bi	As	Ni	Co
Averages. ..	.52 ozs.	.0006%	.0007%	.0006%	None	None	None	None	None



The silver is unusually high in the Trail lead, but with other bullion it has probably averaged about  $\frac{1}{4}$  ounce. By further washing, the silver may be largely reduced, but they find it does not pay to save it.\*

The United States Metals Refining Company, at their plant at Grasselli, produce lead of about the following composition:†

TABLE 104.

Ag	Cu	Sb	Bi	Fe	As	Pb
.00070%	.00100%	.00096%	.00070	.00140%	Trace	99.99524%
= .21 ozs.						

The quality of the lead varies with the skill and experience of the workmen in drawing cathodes and washing them. An inexperienced man is apt to wipe off slime from the anodes on the cathodes in drawing the latter. The following data from Trail, 1902, illustrates this:

TABLE 105.

Cast.	Oz. Ag in Lead.	Cast.	Oz. Ag in Lead.	Cast.	Oz. Ag in Lead.
Aug. 17.....	0.48	Sept. 22	0.43	Oct. 28	0.24
19.....	0.35	24	0.35	30	0.23
21.....	0.26	26	0.18		
23.....	0.17	27	0.30	Nov. 3	0.38
25.....	0.14	29	0.32	5	0.34
27.....	0.26			7	0.38
27.....	0.25	Oct. 1	0.14	10	0.34
29.....	0.20	3	0.15	13	0.35
31.....	0.32	4	0.13	15	0.24
		6	0.22	19	0.22
Sept. 2.....	0.28	8	0.17	19	0.23
4.....	0.19	10	0.17	23	0.20
7.....	0.25	13	0.16	25	0.18
8.....	0.24	15	0.15	28	0.21
10.....	0.28	16	0.10	28	0.22
12.....	0.29	18	0.16		
15.....	0.43	20	0.15	Dec. 1	0.19
16.....	0.45	22	0.11	1	0.12
18.....	0.39	25	0.14		
20.....	0.40	27	0.26	Average	0.25

\* Communicated by the Company.

† Ditto.

The bullion averaged 310.4 ozs. Ag, and 3.15 ozs. Au. The increase in silver about October 27th and November 3d was caused by putting on new men at drawing and washing cathodes, who gradually became accustomed to the work, with a consequent slow reduction in the silver figures.

As showing the unequal distribution of silver in the cathodes, the following data by Dr. E. F. Kern are interesting:

TABLE 106.

	Ag.
Rough sample from center of steel cathode. . . . .	.97 ozs.
Sample from edge of same rough sheet. . . . .	1.64 "
Large warts of lead on steel cathode. . . . .	2.44 "
Smoother cathode from same tank. . . . .	0.23 "
Smooth and bright cathode. . . . .	0.04 "
Smooth heavy cathode. . . . .	0.09 "
Smooth deposit on steel cathode. . . . .	0.07 "

TABLE 107.

## ANALYSES OF REFINED LEAD. TRAIL, 1902.

No.	Cu, Per Cent.	As, Per Cent.	Sb, Per Cent.	Fe, Per Cent.	Zn, PerCent	Sn, Per Cent.	Ag Oz. P. T.	Ni,Co,Cd PerCent.	Bi PerCent
1	0.0006	0.0008	0.0005						
2	0.0003	0.0002	0.0010	0.0010	None				
3	0.0009	0.0001	0.0009	0.0008	"	.....	0.24		
4	0.0016	.....	0.0014	.....	.....	.....	0.47	None	
5	0.0003	.....	0.0060	0.0003	.....	.....	0.22		
6	0.0020	.....	0.0010	0.0046	.....	.....	0.22	None	
7	0.0004	None	0.0066	0.0013	None	0.0035	0.14		
8	0.0004	.....	0.0038	0.0004	"	0.0035	0.25		
9	0.0005	.....	0.0052	0.0004	"	0.0039	0.28		
10	0.0003	None	0.0060	0.0003	"	0.0049	0.43		
11	0.0003	"	0.0042	0.0013	"	0.0059	0.32		
12	0.0005	"	0.0055	0.0009	"	0.0049	0.22		
13	0.0005	"	0.0055	0.0007	"	0.0091	0.11		
14	0.0004	"	0.0063	0.0005	"	0.0012	0.14		
15	0.0003	"	0.0072	0.0003	"	0.0024	0.24		
16	0.0006	"	0.0062	0.0012	"	0.0083	0.22		
17	0.0006	"	0.0072	0.0011	.....	0.0080	0.23		
18	0.0006	"	0.0057	0.0010	.....	0.0053	0.34		
19	0.0005	"	0.0066	0.0016	.....	0.0140	0.38		
19	0.0005	"	0.0044	0.0011	.....	0.0108	0.35		
20	0.0004	"	0.0047	0.0015	.....	0.0072	0.22		
20	0.0004	"	0.0034	0.0016	.....	Trace	0.23		
21	0.0022	"	0.0010	0.0046	None	0.0081	0.38	None	None

TABLE 108.

ANALYSES OF REFINED LEAD. TRAIL, 1903 OR 1904.

Silver, Per Cent.	Copper, Per Cent	Lead, Per Cent.	Iron, Per Cent.	Antimony, Per Cent.	Tin, Per Cent	Bi,Co,Ni,
.00129	.0015	.....	.0015	.....	.0148	Nil
.00129	.0005	99.996	.0015	.0006	Trace	"
.0015	.0011	99.976	.0015	.0003	"	"
.00030	.0014	99.995	.0015	.0006	"	"
.00192	.0005	99.995	.0017	.0003	"	"
.00077	.0010	99.997	.0013	Trace	"	"
.00084	.0020	99.995	.0015	.0003	"	"
.00091	.0007	99.996	.0015	.0009	"	"

TABLE 109.

ANALYSES OF REFINED LEAD. TRAIL, 1904.

Letter from Mr. W. H. Aldridge.

Silver, Per Cent.	Copper, PerCent	Lead, Per Cent.	Iron, PerCent	Tin, PerCent	Anti- mony, Per Cent.	Arsenic, PerCent	Bi, PerCent	Zinc, PerCent
.0013 = .38 ozs.	.00075	99.9938	.00075	.0001	.0028	None	None	.0005
.0017 = .50 "	.001	99.9930	.0012	.0001	.0026	"	"	.0004
.0019 = .55 "	.0009	99.9943	.0007	.0001	.0017	"	"	.0004

TABLE 110.

ANALYSES OF BULLION. TRAIL, 1902.

No.	Fe, PerCent	Cu, PerCent	Sb, PerCent	Sn, PerCent	As, PerCent	Ag, PerCent	Au, PerCent	Pb, PerCent	Ag Oz. P. T.	Au Oz P. T.
1	0.0075	0.1700	0.5400	0.0118	0.1460	1.0962	0.0085	98.0200	319.7	2.49
2	0.0115	0.1500	0.6100	0.0158	0.0960	1.2014	0.0086	97.9068	350.4	2.52
3	0.0070	0.1600	0.4000	0.0474	0.1330	1.0738	0.0123	98.1665	313.2	3.6
4	0.0165	0.1400	0.7000	0.0236	0.3120	0.8914	0.0151	97.9014	260.0	4.42
5	0.0120	0.1400	0.8700	0.0432	0.2260	0.6082	0.0124	98.0082	177.4	3.63
6	0.0055	0.1300	0.7300	0.0316	0.1030	0.6600	0.0106	98.2693	192.5	3.10
7	0.0380	0.3600	0.4030	.....	Trace	0.7230	0.0180	98.4580	210.9	5.25



TABLE 111.

## SLIME ANALYSES.

No.	Anodes.	Cu, PerCent	Ag, PerCent	Sb, PerCent	As, Per Ct.	Pb, Per Ct.
1	Lead, Trail, B. C. ....	8.83	28.15	27.10	12.42	17.05
2	Lead, Trail, B. C. ....	22.36	23.05	21.16	5.40	10.62
3	Lead, Monterey, Mexico. ....	1.90	32.11	29.51	9.14	9.05
4	Lead, Mexican. ....	9.30	4.7	25.32	44.58	10.30
5	Lead, Mexican. ....	6.38	3.90	50.16	15.23	5.30
6	Lead, Trail, B. C. ....	1.40	31.62	35.71	4.91	9.57
7	Lead, Trail, B. C. ....	6.60	32.21	24.60	2.20	12.60
8	Rich lead, Parkes process. ....	12.56	78.45	4.12	.....	3.00
9	Lead, Trail, B. C. ....	7.10	29.20	30.50	6.10	10.20
10	Lead, Trail, B. C. ....	7.70	31.90	37.60	2.80	12.60
11	Lead, Trail, B. C. ....	8.1	14.6	27.6	7.0	16.0
12	Lead from El Doctor Mine, Mexico. ...	7.82	2.44	75.34	0.24	12.23
13	Copper, Montana converter anodes. ...	41	24			
14	Copper, Montana reverberatory anodes	18	51.4			
15	Copper, Boston and Montana. ....	57	14.80	2.00	2.60	5.26
16	Copper, Boston and Montana. ....	53.29	12.90	3.30	1.15	Tr.

No.	Anodes.	Bi, PerCt.	S, PerCt.	Fe, PrCt.	Oz. Au.	Se, PrCr.	Te, PrCt.
1	Lead, Trail, B. C. ....	Nil	.....	1.27			
2	Lead, Trail, B. C. ....	Nil	.....	1.12			
3	Lead, Monterey, Mexico. ....	Tr.	.....	.49	29.1		
4	Lead, Mexican. ....	.52					
5	Lead, Mexican. ....	19.74	Nil	Nil			
6	Lead, Trail, B. C. ....	.....	.....	.....	180.33		
7	Lead, Trail, B. C. ....	.....	.....	.....	81.99		
8	Rich lead, Parkes process. ....	.88					
9	Lead, Trail, B. C. ....						
10	Lead, Trail, B. C. ....						
11	Lead, Trail, B. C. ....	0.81	.....	1.35	34.5		
12	Lead from El Doctor Mine, Mexico. ...	1.95					
13	Copper, Montana converter anodes. ...	.....	.....	.....	18		
14	Copper, Montana reverberatory anodes	.....	.....	.....	38		
15	Copper, Boston and Montana. ....	5.70	.....	.....	.....	2.0	1.00
16	Copper, Boston and Montana. ....	1.55	11.96	.....	.....	.26	1.97

REMARKS.—1, 2. Trans. Am. Inst. Min. Eng., 1904, p. 182. 3, 4. Trans. Am. Inst. Min. Eng., 1904, p. 183. 5. Original. 6, 7. Mines and Minerals, Vol. 25 (1905), p. 288. 8, 9, 10, 11, 12. Original. 13, 14. Trans. Am. Inst. Min. Eng., 1904, p. 310. 15, 16. Original.

TABLE 112.

ANALYSES OF BULLION AND REFINED LEAD. TROY, N. Y.

	Ag, Per Cent.	Cu, Per Cent.	Sb, Per Cent.	Pb, Per Cent.
Bullion. ....	0.50	0.31	0.43	98.76
Refined lead. ....	0.0003	0.0007	0.0019	99.9971

TABLE 113.

ANALYSES OF BULLION AND REFINED LEAD. TROY, N. Y.

	Cu PerCent	Bi PerCent	As PerCent	Sb PerCent	Ag Oz. P. T.	Ag PerCent	Au Oz. P. T.	Fe PerCent	Zn PerCent
Bullion. ....	0.75	1.22	0.936	0.6832	358.89	.....	1.71		
Refined lead. .	0.0027	.0037	0.0025	0.0000	.....	0.0010	None	0.0022	0.0018

TABLE 114.

ANALYSES OF BULLION, REFINED LEAD AND SLIMES. TROY, N. Y.

	Pb Pr Ct.	Cu PerCent	As Per Cent.	Sb Per Cent.	Ag Oz. Per T.	Ag Per Cent.	Fe, Zn, Ni Co, Pr Ct.	Bi
Bullion. ....	96.73	0.096	0.85	1.42	about 275			
Refined lead. .	.....	0.0013	0.00506	0.0028	.....	0.00068	0.0027	Tr.
Slimes (dry sample). ....	9.05	1.9	9.14	29.51	9366.9	.....	0.49	"

TABLE 115.

ANALYSES OF BULLION, REFINED LEAD AND SLIMES. TROY, N. Y.

	Pb Per Cent.	Cu Per Cent.	Bi Per Cent.	Ag Per Cent.	Sb Per Cent.	As Per Cent.
Bullion. ....	87.14	1.40	0.14	0.64	4.0	7.4
Lead. ....	.....	0.0010	0.0022	.....	0.0017	Trace
Slimes. ....	10.3	9.3	0.52	4.7	25.32	44.58

The following analyses by the Osaka Technical Analyzing Department, presumably of lead in the Japanese market, probably give a good idea of the present quality of commercial lead in the world's markets:

TABLE 116.

## Pig LEAD ANALYSES.

By the Osaka Technical Analyzing Department.

Per Cent.	Selby.	Trail.	Smelter.	English Chemical.	B. H. P.	Enthoven
Lead. ....	99.9579	99.9890	99.9762	99.9693	99.9853	99.9851
Insolubles. ....	0.0040	Trace	Trace	Trace	Trace	Trace
Bismuth. ....	0.0300	None	0.0046	"	None	0.0048
Cadium. ....	Trace	"	0.0002	0.0007	Trace	Trace
Nickel. ....	0.0001	Trace	Trace	0.0003	None	"
Cobalt. ....	None	None	"	Trace	Trace	"
Silver. ....	0.0010	0.0025	"	0.0020	0.0009	0.0015
Manganese. ....	0.0008	None	0.0003	None	None	None
Copper. ....	None	0.0003	None	0.0097	"	"
Antimony. ....	"	None	0.0137	0.0149	0.0108	0.0160
Tin. ....	0.0004	0.0007	None	None	0.0004	None
Arsenic. ....	0.0024	0.0020	0.0090	0.0002	None	"
Zinc. ....	0.0003	0.0002	Trace	Trace	0.0001	Trace
Iron. ....	0.0027	0.0053	0.0039	0.0029	0.0025	0.0026

NOTE.—Selby and Smelter are American; Trail, Canadian; Enthoven and Chemical, English; B. H. P., Australian.



## CHAPTER IX.

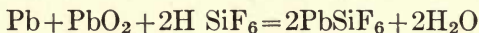
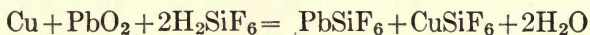
### TREATMENT OF LEAD CONTAINING BY-PRODUCTS.

THE refining of copper-lead alloys with high copper is of some importance. First, because such alloys can be produced as "bottoms" from copper-lead matte, and a method of saving both lead and copper is then provided. Second, because some lead bullions give a good deal of dross in remelting which can not very well be stirred into the lead to make a uniform anode, and the natural method of treating such drosses, containing as they do from 80% to 90% lead or more, is to get them into some kind of an anode and extract the lead electrolytically in the usual manner.

Dr. E. F. Kern tested many methods of treatment in my laboratory using an alloy of 60% Pb, 39% Cu, and 1% Ag, which methods included removing of the lead by the combined action of fluosilicic-acid solution and air, the alloy losing 2% in twenty-one hours. The alloy was also ground up, mixed with broken electrolytic lead peroxide, and let stand three and one-half days with solution containing lead fluosilicate and fluosilicic acid. At the end of that time all the lead had dissolved out, as well as some copper, leaving a porous copper material of the same shape as the original pieces of alloy. Some  $\text{PbO}_2$  remained, the execution of the experiment being faulty in not using the right amount of

$\text{PbO}_2$  to either dissolve the lead alone, or both the lead and copper.

The chemical reactions are:



This method would not be a promising one, although the lead, or lead and copper dissolved, as well as the lead peroxide and the fluosilicic acid, could be recovered by electrolyzing the solution with metal cathode and carbon anodes. When this is done, lead peroxide deposits on the anodes as a hard, greenish black, lustrous, well-conducting deposit of a smoothness superior to most metallic deposits. The reactions are the reverse of those just given. The electromotive force when depositing lead is about 2.1 volts, and 1.7 volts when depositing copper.

The alloy, or a very similar one, was also treated with a solution of ferric fluosilicate which dissolved out the lead, and also traces of copper, from using a little too much ferric salt. The residue retained the original shape of the alloy, but was very soft and porous, consisting of copper and silver. In this process the solution was to be electrolyzed for the lead and recovery of the ferric fluosilicate.

Far the best method consists in treating the alloy as anode in the usual lead-depositing solution, with a somewhat smaller current density.

In one experiment the following data were noted: Current density about 12.5 amperes per square foot. Distance between electrodes 1 to 2 inches. Volts about .15 to .20, rising later to .42 volts, when slime had to be removed. Solution

4% Pb, 15%  $\text{SiF}_6$ . The anode was 1 inch thick and the slime had to be removed several times before the anode was completely decomposed.

TABLE 117.

Weight anode. ....	1778 gr.
Lead deposited. ....	732 gr.
Slime. ....	340 gr.
Alloy remaining. ....	675 gr.

Dr. Kern put 85 gr. of the slime in a small lead box with perforations in the sides, and electrolyzed it with a solution containing 20%  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 5%  $\text{H}_2\text{SO}_4$ , with copper cathodes.

As the slime settled down 50 gr. more were added, making 135 gr. used altogether. Electromotive force .2 volts; copper deposited 100 gr.; weight of residue of silver and lead sulphate 37 gr.

Analysis of these figures indicates the following: 135 gr. slime result from about 475 gr. of the alloy. The slime contains then 4 gr. silver and 33 gr. lead sulphate, perhaps a little of this coming from the lead box which lost a little in weight. As a result, practically all the copper was recovered, but 8.8% of the lead was apparently converted into lead sulphate. Perhaps some of this apparent loss was due to insufficient washing of the slime.

In the aggregate the quantity of copper dross converted into matte by resmelting, must be quite large, and the lead lost in the final conversion of the copper-lead matte is well worth saving. Refiners could very well treat their drosses by casting into anodes at a red heat and extracting the lead electrolytically.

Experiments on refining hard lead with 18.8% Sb, and



rich lead from the Parkes or Pattinson processes, are described in Chapter I. The antimony slime could be refined direct with the antimony fluoride solution, as it retains considerable mechanical strength, or it could be cast into anodes.

The electrolytic lead process ought to be of advantage in a small way in some other branches, as for instance refining the lead-gold bullion produced in cyanide mills.

Experiments on galena direct have been fruitless.

Electrolytic refining of lead bullion high in bismuth, is practiced on a small scale, primarily to produce bismuth.

Table 118 gives the composition of various alloys which have been successfully refined, producing pure lead at the cathodes. Table 25, on page 68, gives a number of others refined by Senn.\*

TABLE 118.  
ANALYSES OF LEAD ANODES.

Pb	Cu	Sb	As	Ag	Bi	Current Density Per Sq. Foot.	Slime Contains.
88. %	1.53%	.5 %	.....	9.75%	1.11%	7 amps.	
82.37%	2.22%	.77%	.....	14.60%	.19%	7 "	
65.37%	.....	19.51%	5.85%	1.95%	7.32%	2.0 "	5.3% Pb
65.56%	1.94%	18.24%	5.47%	1.94%	6.94%	2.0 "	
82.79%	.97%	9.12%	2.73%	.97%	3.42%	2.0 "	
88.52%	.68%	6.08%	1.82%	.68%	2.28%	2.0 "	
60 %	39.0%	.....	.....	1.0 %	.....	4-7 "	
87.14%	1.40%	4.10%	7.40%	.64%	0.14%	11.6-17 "	10.3%

\* Zeitschrift. für Elektrochemie. 1905. Vol. XI., page 229.

## CHAPTER X.

### ANALYTICAL METHODS AND EXPERIMENTAL WORK.

**Slime.**—Dissolve 1 gr. in HCl and  $\text{KClO}_3$ , boil out chlorine, add a little water, neutralize with dry sodium carbonate, add excess of  $\text{Na}_2\text{S}$  solution (prepared from caustic soda by saturating with  $\text{H}_2\text{S}$ , then adding another portion of caustic soda of same amount, and allowing to settle before using). Heat on plate for an hour or so, filter, add 2 to 3 gr. pure caustic soda or potash, and determine Sb electrolytically.

The following remarks will be useful in making electrolytic antimony determinations. If you are using a smooth platinum cathode, deposit on it a layer of antimony from a fairly strong solution of tartar emetic to which a little nitric acid has been added, and the precipitated  $\text{Sb}_2\text{O}_3$  redissolved by adding tartaric acid. Use a current of about 1 to 2 amperes per square foot in preparing the cathode, which is then washed with water, dried and weighed.

The antimony deposits from the sulphide solution made as above on the prepared cathode in a beautiful, smooth condition fit for accurate determinations. I usually start the electrolysis cold with a current of  $\frac{1}{2}$  ampere for a cathode having 20 square inches of surface, and heat the solution up while the current is on to  $70^\circ$  and increase the current to  $1\frac{1}{2}$  to 2 amperes. After about three hours turn off the heat, and after cooling remove cathode, plunge into distilled water with-



out interrupting the current, wash, dry, and weigh. The use of alcohol in drying is of no advantage, as the antimony does not oxidize very readily anyway. I have found the same weight either way.

Add dilute  $\text{H}_2\text{SO}_4$  to filtrate, heat, filter off  $\text{As}_2\text{S}_3 + \text{S}$ , add fairly dry paper and precipitate to about 40 cc. concentrated  $\text{HNO}_3$ , and digest gently on plate for six to eight hours while acid is slowly driven off. This removes small amounts of chlorine and all paper. Determine As by Pearce's silver arsenate method, described in numerous books.

For copper, silver, bismuth, iron, and lead I have taken a separate sample, dissolved in nitric and tartaric acids, neutralized with soda, added  $\text{Na}_2\text{S}$  digested and filtered. Possibly the solution running through is equally suitable for determining arsenic and antimony, though several failures, perhaps due to other reasons, have always prevented successful results so far.

The insoluble sulphides with the filter paper are dried placed in a small beaker, a light applied, when the paper burns off and carbonizes. Concentrated  $\text{H}_2\text{SO}_4$  is added and gently boiled, cover on, till carbon is all gone and solution is clear greenish. Possibly sodium or potassium bisulphate would work quicker.

After cooling add water and pass  $\text{H}_2\text{S}$ . Filter off iron, determine it by boiling  $\text{H}_2\text{S}$  from filtrate, and titrating with permanganate. Redissolve sulphides in  $\text{H}_2\text{SO}_4$  in same way again. Then neutralize with soda and add KCN free from sulphide. Pb and Bi remain insoluble as carbonates, while silver and copper dissolve.

The silver and copper cyanide solution, may be acidified, AgCN filtered off, and copper determined electrolytically. I



have, however, got good results by electrolyzing the solution for silver, using a single dry battery, giving 1.3 volts about as a maximum, for source of current. Time required about four or five hours, if solution is warm. Then acidify solution with nitric acid under the hood, evaporate down, to remove the HCN and determine copper electrolytically. Copper and silver can also be determined separately, the first by dissolving 1 gr. of the slime in nitric acid, removing silver as chloride, precipitating with ammonia, filtering and titrating with KCN, while silver will often be determined in a works by assay.

The bismuth and lead carbonates obtained as above are dissolved in dilute nitric acid, the solution is almost neutralized with ammonia, heated, and a few drops of HCl added to throw out BiOCl (Ledoux's method \*), which can be dried and weighed at 100° in a Gooch crucible. A convenient and satisfactory filter for a Gooch crucible consists of a small disc of filter-paper, the same size as the bottom of the crucible.

Add sulphuric acid to the filtrate from BiOCl, and evaporate for lead sulphate, which may be determined in several familiar ways.

The analysis of metallic antimony can be made in the same way as the analysis of slime given above, omitting the separation and determination of elements known to be absent.

**Assay of dore bullion.**—The method in general use in the refineries and assay offices of this country is about as follows: The determination of silver is carried out by Gay-Lussac's method of precipitation with salt, although Volhard's method, using a standard solution of thiocyanate, gives good results unless there is considerable copper present.

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\* Low, "Technical Methods of Ore Analysis," page 55.

*Gold.*—5 gr. are digested in a porcelain crucible about 2 to 2½ inches high, with one to six nitric acid, until solution ceases. The solution is decanted, nitric acid one to one added, and boiling continued until gold changes color. It is then washed with hot water several times, dried and weighed. I understand at the San Francisco mint 400 parts of gold are added to the assay for gold, and a check made up containing 400 parts of gold. This is then cupelled with lead and parted with acid and weighed, and the surcharge, or silver remaining in the gold, determined from the check.

To determine gold accurately a proof should be run, using a made-up alloy containing gold, silver, and copper, in about the same proportions as known to exist in the doré, cupelling with an equal amount of lead, and parting the button and weighing the gold in the same manner. This is done at the Philadelphia mint.

Sampling doré bullion may be done by melting in a graphite crucible, stirring well, pouring off; after one-third and two-thirds are about poured off, collect a small sample by putting small crucibles in stream of metal. Both samples are granulated separately and assayed separately. If they do not agree the bar is melted over again.\*

**Analysis of refined lead.**—Five hundred gr. of lead are cleaned and hammered or rolled into thin plates, being very careful to use a perfectly clean and bright hammer and anvil to avoid introducing iron into the sample. The lead is dissolved in a large beaker on the hot plate, in 500 cc. nitric acid 1.42 and 1,000 cc. water. If the solution gets too hot it will foam very much and run over, so that it is necessary to watch

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\* Selby Smelting and Lead Company.

it until most of the lead is dissolved. For the same reason rolling or hammering the lead into very thin strips is not desirable.

After all the lead is dissolved the solution is generally perfectly clear, although if more than .02-.03% of antimony or any tin is present, it will show some turbidity.\* The solution should be diluted to nearly 2 litres to prevent lead nitrate crystallizing out on cooling. If not perfectly clear it is filtered into a 2-litre measuring flask, otherwise it is merely transferred thereto. 145 cc. concentrated sulphuric acid, previously diluted with water, are added, and the flask filled to the mark. After settling 1,700 cc. of clear solution are secured by pouring through a large filter. 100 gr. of lead as sulphate occupy 23 cc., so that we have in solution  $\frac{1700}{23}$  of the impurities in 500 gr. of lead = 451 gr. lead.

The 1,700 cc. are evaporated to fumes of  $\text{H}_2\text{SO}_4$ , taken up with 50 cc. water, and the lead sulphate filtered off. The lead sulphate is digested with pure sodium sulphide solution, filtered and added with the other sodium sulphide solution obtained further on. The filtrate from the lead sulphate is treated hot with  $\text{H}_2\text{S}$  for some time and the gas passed through until cold. After settling completely it is filtered, and iron and zinc determined in the filtrate, while the sulphides are treated with  $\text{Na}_2\text{S}$ . Determine antimony and arsenic as described under slime analysis.

The insoluble sulphides of lead, bismuth, copper, and silver may be dissolved in nitric acid, neutralized with sodium carbonate, and KCN added. Lead and bismuth carbonates are filtered off, the filtrate acidified with  $\text{H}_2\text{SO}_4$  under the hood,  $\text{AgCN}$  filtered off and the solution boiled to expel all

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\* "Quantitative Chemical Analysis by Electrolysis." Classen-Herrick-Boltwood 265.



HCN, after which copper is determined in the solution as follows: Nearly neutralize the solution with ammonia, keeping the bulk small, say 50 cc., add ammonium acetate, and divide into two equal parts. Add to one part a fair excess of potassium ferrocyanide solution, and filter off the red precipitate immediately, passing through the paper twice if necessary. Add 1 cc. acetic acid to each and the same amount of potassium ferrocyanide to the unfiltered half, and match the color in the filtered half by adding a weak copper sulphate solution of known strength from a burette, allowing one minute between each addition of copper sulphate, for the color to develop.\*

The silver cyanide precipitate is not desired, for silver is determined by cupelling a separate sample of the lead.

To determine bismuth, dissolve the carbonates of lead and bismuth in dilute nitric acid and precipitate as  $\text{BiOCl}$ , by Ledoux's method, as described under "Slime."

To be sure of the results it is necessary to run a check analysis on the nitric and sulphuric acids, evaporating the same amount of them down nearly to dryness, and treating the last of the sulphuric acid in the same way as the lead sample.

The results of refined lead analysis are more apt to depend on the chemist than on the lead, and it is desirable that as many errors as possible be eliminated to get accurate results. One of the causes of error is in the chemicals used, which are not absolutely pure of course, and import certain quantities of iron, copper, arsenic, and antimony. The amount of nitric and sulphuric acid used is as great as the lead sample, so that

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\* Crooke's "Select Methods of Chemical Analysis," page 338.

a check should be run on the acids. On one occasion I determined copper in lead as .0010%, but on running a check on the acid, it was discovered that there was no copper in the lead, but it all came from the chemicals.

The following show the variation of results on the same sample of electrolytic lead:

TABLE 119.

Fe	Zn	Sb	Cu	As	Bi	Ag	Chemist.
.00023%	.0004%	.0007%	.00043%	.00005%	None	.00003%	Betts
.00032%	.....	.....	.00045%				
.00040%	.....	.....	.00045%				
.0022 %	.0079%	.0013%	.0013 %	.0065 %	.....	.00016%	New York No. 1
.0037 %	.0042%	.0007%	.0012 %	.0092 %	.....	.0003 %	New York No. 2

As the lead was deposited electrolytically and could have contained no zinc, the figures by 2 and 3 are certainly wrong. My iron and copper determination was made in triplicate and all results agreed fairly well, especially for copper. There is no agreement at all for arsenic and silver, but I have no confidence in my own figures for these elements. As it would be easy to introduce traces of iron into the sample, unless hammered or rolled with care, I think my own figures are nearer right. The same remark applies to the presence of iron in the lead as to zinc. As the precipitated lead sulphate may take out some antimony, the figures for Sb .0007% by two chemists are apt to be slightly too low.

The following analyses were made in the same sample, one at Trail, by Dr. Wm. Valentine, and one by Messrs. Ledoux & Co., of New York.

TABLE 120.

Cu	Sb	Fe	Sn	Ag	
.0003%	.0060%	.0003%	.0049%	.0006%	Valentine Ledoux & Co.
.0020%	.0010%	.0046%	.0095%	.0006%	

The agreement in the case of silver is satisfactory. The lower figures for iron and copper show less contamination of the sample mechanically or by chemicals, Dr. Valentine's  $\text{Sn} + \text{Sb} = 0.105\%$  and Ledoux & Co.'s  $\text{Sn} + \text{Sb} = .0109\%$ , so that the separation was probably not complete in one case.

Antimony, arsenic, and tin are determined by us in the sulphide solutions by electrolysis. Antimony only is removed when the solution is electrolyzed. This is an accurate method.

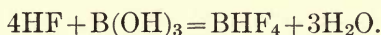
**Slag from fusing slime.**—This contains antimony, arsenic, lead, bismuth, copper, iron, silica, and sulphur. Dissolve in  $\text{HCl}$ , add  $\text{KClO}_3$ , boil out chlorine, neutralize with sodium carbonate, and determine antimony and arsenic, as in making slime analyses. The insoluble sulphides may also be further analyzed as in the slime analysis.

**Electrolyte.**—To determine acidity, the following method was in use at Trail. Add an equal volume of alcohol to the sample and titrate with  $\text{KOH}$  and phenolphthalein, correcting for iron and alumina. To determine lead add  $\text{H}_2\text{SO}_4$ , filter and determine lead by the molybdate method. The following method is used in my laboratory: Add alcoholic potassium acetate solution. Filter off  $\text{K}_2\text{SiF}_6$ , wash with diluted alcohol, add paper and precipitate to distilled water in a beaker, heat to boiling and titrate with  $\text{NaOH}$ , using rosolic acid preferably,



but also phenolphthalein as indicator. Lead is determined as described above. Also the analysis may be made by adding neutral ammonium sulphate, filtering and determining lead sulphate. Titrate filtrate with cochineal and standard ammonia in the cold. Other determinations on electrolyte are seldom made. For free HF, add to hot solution, hot boric acid of known strength until a permanent precipitate of silica results.

Reaction:



Also remove lead with  $\text{H}_2\text{S}$  filter, let stand till  $\text{H}_2\text{S}$  has passed off or oxidized, and determine HF and  $\text{H}_2\text{SiF}_6$  as described under the analysis of fluosilicic acid, page 177.

**Copper-silver matte from melting slime.**—To determine sulphur, dissolve in concentrated nitric acid. All or nearly all of the sulphur oxidizes. Dilute and filter. Remove silver from filtrate with HCl, add filtrate to insoluble portion, add  $\text{KClO}_3$  and evaporate to dryness. Add HCl, to dissolve salts, then add ammonia until slightly alkaline, and filter. Add HCl and  $\text{BaCl}_2$  to filtrate. To determine lead, copper, and silver dissolve 1 gr. in boiling concentrated sulphuric acid, cool, dilute, filter off  $\text{PbSO}_4$  and titrate by Alexander's molybdate method. Determine silver in filtrate with  $\text{NH}_4\text{CNS}$  solution, filter, add ammonia, filter, and determine copper in filtrate with KCN. To determine antimony fuse 1 gr. in porcelain crucible with 3 gr. sulphur and 4 gr. sodium carbonate, take up in water, filter, add  $\text{H}_2\text{SO}_4$  to precipitate sulphides, dissolve sulphides in HCl and  $\text{KClO}_3$ , boil out chlorine, reduce with sodium sulphite, boil out  $\text{SO}_2$  and titrate with permanganate. In determining antimony in the chloride solution by



permanganate, the solution should be cool and of considerable volume, and must contain enough HCl to prevent the formation of a brown color on adding permanganate and not enough to decompose permanganate fast enough to interfere with the end point. In reducing with sodium sulphite, I add the sodium sulphite to the solution containing say  $\frac{1}{2}$  to  $\frac{1}{3}$  strong HCl, and heat to boiling very slowly to give the SO<sub>2</sub> plenty of time to act. Then boil off say  $\frac{1}{3}$  the total volume, cool, dilute somewhat, perhaps adding HCl, and titrate. To make sure of the result more sodium sulphite and HCl may be added after finishing the titration, solution gradually heated, then boiled and titrated again.

**Method of determining silica in slime.**—Five gr. of slime is treated with moderately strong HNO<sub>3</sub> and boric acid, filtered, silver precipitated by HCl, evaporated to dryness several times with HCl. The residue from the nitric acid was dissolved in HCl and solution evaporated to dryness several times with HCl. Both of these evaporations were taken up with HCl and the insoluble material filtered off. The residue of the slime from the treatment with HCl was treated with aqua regia and insoluble material filtered off. All the insoluble matter was ignited together, weighed, pure HF added, HF and H<sub>2</sub>SiF<sub>6</sub> driven off, and residue weighed again, calling the difference silica.

**Antimony fluoride solution.**—It is frequently convenient to titrate this with permanganate, after diluting the sample with water and HCl. If a strong yellow color develops, the result is too high, and the proportion of HCl was not high enough, or the sample was too concentrated. The solution can be standardized against ferrous iron; 56 parts iron=60 parts antimony.

**Experimental work.**—Preparation of fluosilicic acid. Put hydrofluoric acid 15–20% strength in a lead pan and add excess of finely powdered calcined flint, which dissolves more readily than quartz. Heat, but not to boiling, until solution is saturated with silica, or until pungent smell of HF has stopped coming off. To make the lead solution, add the right amount of white lead, which ordinarily contains 80% of metallic lead. Gelatine or glue is added to the electrolyte in the form of a strong, hot solution in water.

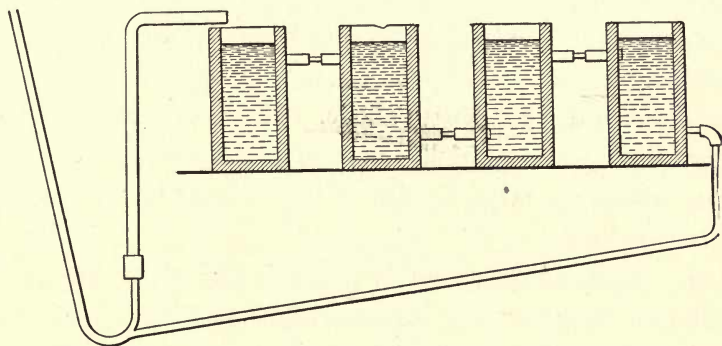


FIG. 66.

Small electrolytic tanks can be conveniently made of wood, and soaked or dipped in hot paraffine for some time. After cooling a layer of paraffine can be put on the wood by letting it cool inside, then adding paraffine and turning the box in various positions. This makes a good tank for refining experiments.

To provide circulation, arrangements for experiments as shown in Fig. 66 are convenient. The tanks are rectangular and conditions as to current density, voltage, solution, temperature, products, etc., may be as exactly determined as on a large scale.



Conductivity measurements are made with sufficient accuracy for practical purposes, by using a small paraffined box about 3 inches square and deep, with two pure lead sheets at each end. If the width of the box is known and the volume of the solution is measured, the cross-sectional area can be calculated. Current is passed through while the solution is stirred, and the resistance calculated from the ammeter and voltmeter readings. As the polarizing e.m.f. in depositing lead is under .02 volt, the method is sufficiently accurate.

In antimony depositing with lead rods as anode, practical work may be duplicated with one anode by using a tall paraffined box with a full-length anode. The box is about 3 inches square inside, and faithfully represents a full-size tank, which comprises only a large number of the same units, without the intervening walls.

In experimenting on small quantities of slime it can be cooked up with solutions in porcelain evaporating dishes. For 10 or 20 lbs. large stoneware crocks holding 60–80 litres are good. Steam can be turned in through a lead pipe for heating and stirring. Antimony fluoride solutions can be handled in painted lead tanks or paraffined wooden ones. To roast slime with sulphuric acid it is sufficient to spread it on a cast-iron plate heated underneath.

For ferric sulphate electrolysis on a small scale a tank, as shown in Fig. 67, taking 25–50 amperes is useful. The anodes are cast in lead in a slit cut in a board, and hung with two narrow boards from the ceiling. For work lasting only a few weeks the lead tank and diaphragm can be soldered together with coarse solder, 2 or 3 parts of lead to 1 of tin.

For reduction of lead-antimony slags, use a lead pan in which the slag is spread out and made cathode with a sheet-lead plate for anode just above the cathode. For reduction in the fused

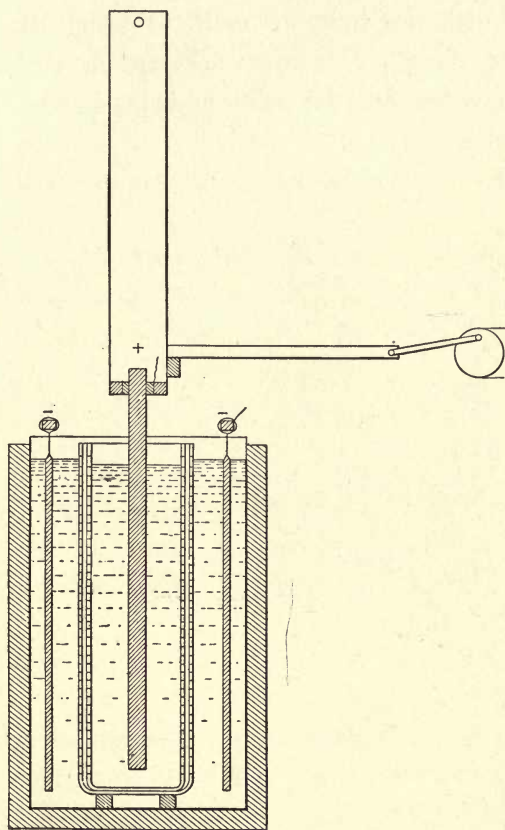


FIG. 67.

state lead chloride (from precipitating lead nitrate or acetate with  $\text{NaCl}$ ) is melted in a porcelain crucible, and two carbon electrodes dipped in. The reduced metal drops from the negative electrode to the bottom of the crucible. It is necessary to

have the crucible well covered to keep the air out. The slag is fed from time to time as reduced.

An experimental tank for one full-sized lead anode, about 6 inches wide, 30 inches long, and 42 inches deep, with one glass end, was built at Trail, to watch the behavior of the anode slime. This was not successful in that particular instance because the solution happened to be too dark and turbid.



## CHAPTER XI.

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## APPENDICES.

### APPENDIX I.

#### PLANT OF THE CONSOLIDATED MINING AND SMELTING COMPANY OF CANADA, LIMITED, AT TRAIL, BRITISH COLUMBIA.

THE pioneer electrolytic lead refinery is that of the above company, which is located on the west bank of the Columbia River a few miles north of the international boundary. Trail has railroad connection with Rossland, which in turn is reached by the Great Northern Railroad, and is also connected with the Canadian Pacific system at the north.

The Trail plant has been operated since 1902, with some interruptions for enlargements, and has a present capacity of 80 tons per day, although the bullion received to be treated at present amounts to only about 45 tons per day. It will probably be only a short time before sufficient lead will be locally produced to keep the plant running at its full capacity. The operations and plant have been brought to a high standard by the capable management, and many good points have been developed that should be noted.

Power is supplied by the West Kootenay Light and Power Company from their plant at the Bonnington Falls, about 25 or 30 miles north, in the form of three-phase sixty-cycle current, I believe at 22,000 volts. It is transformed to 550 volts at a sub-station about a quarter of a mile from the refinery,

and near the smelter. At the refinery power plant there is a Canadian General Electric 600 H.P., 60-cycle, 550-volt motor directly connected to a 3600-ampere, 60-110 volt electrolytic generator of the same make, which supplies power to the lead-depositing tanks. A Westinghouse 165 H.P., 550 volt, three-phase motor is directly connected to a 105 K.W., 30-volt, 3500-ampere, 580-rpm. electrolytic generator of the same make, which at present supplies current to the electrolytic antimony-depositing tanks. For power purposes there is a 20 K.W., 125-volt direct-current generator that supplies power to the crane. The crane uses about 2 H.P. when running. The pumps require 2-3 H.P., using a three-phase motor, and the centrifugal lead-pumps use about 3 H.P. each against a six-foot head of lead. Probably the average power in use for power purposes does not reach 5 H.P. and the maximum in use is about 12 H.P.

The tank-room 50 feet wide and 315 feet long is subdivided about as follows: Adjoining the south end there is a room about 18 by 40 feet in which the cathodes are hung and straightened. In the main building is first a clear space of about 4 feet from the wall; next comes a block of 132 tanks occupying a length of about 96 to 97 feet. These tanks are in six double cascades, 11 tanks long, the highest tanks being 47 inches and the lowest 20 inches above the floor, which is level.

At the low end of these tanks is a small space for solution launders, and then comes a row across the building of cleaning-tanks, 7 feet 6 inches long and 6 feet 3 inches wide. Then comes a 17-foot clear space with a floor of cast-iron plates. This space is used for electrode storage, the electrodes resting on small cars, and also for working space. Then there is another row of six washing-tanks of the same size, followed by a three-foot space for launders and bus-bar connections, and a

block of 72 tanks in six-tank cascades which occupies 54 feet of the length of the building. Then there is a three-foot space for launders and bus-bar connections, followed by 60 tanks in five-tank cascades=44 feet. These latter tanks have not yet been used on account of the present scarcity of bullion to be treated, though they are going to be put in commission soon, while the current flowing will be reduced as long as the shortage of bullion lasts. Instead of using less than the full number of tanks, all the tanks will be worked with a smaller current. Then there is a set of electrode storage racks about 16 feet long, which occupy the full width of the building, excepting the aisles.

The remainder of the building is occupied by the melting floor and contains the lead and bullion kettles and casting floor. In a small side room is the apparatus for making starting sheets. There is also in one corner a lead-pipe machine. The floor is subdivided into first a 25-foot clear space to the lead kettles, then the lead kettles take 12 feet. Then there is another twenty-five foot clear space to the bullion kettles, which are placed toward one side of the centre of the building and occupy 12 feet of its length, with a final space at the end of about 18 feet.

The tanks are of four-inch fir with bolts passing through the wood and are similar to Fig. 38. Mr. John F. Miller has described to me his method of lining tanks.\* He uses two grades of California asphalt, "hard" and "D" grade. These are mixed in the proportions required to give a melting point of 45° C. Mr. Miller determines the melting points of the

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\* Mr. Miller has applied for United States patents on his tank and method of lining it.



mixtures by molding them into cones about 4 inches high, and keeps them in a water-bath of a certain temperature for twenty-four hours. If the cone does not show any alteration in shape in that time, the melting-point is some higher temperature, and if it runs at all, the melting-point is some lower temperature.

The seams of the tank are made as shown in the sketch (Fig. 68). The tank is placed in various positions, the side being treated being of course horizontal. The seam is first

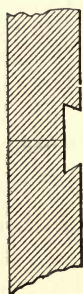


FIG. 68.

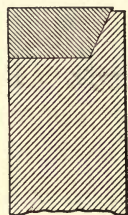


FIG. 69.

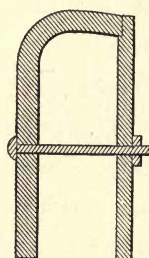


FIG. 70.

filled with several layers of asphalt by running along the seam with a teakettle holding the hot mixture. After the seams are all filled on that side, it is then flooded with an asphalt layer about one-quarter inch thick. Two men can line two double tanks per day. The tanks in the refinery are giving excellent satisfaction. Though in use two years they have not yet required any repairs. There is little or no absorption of the solution by the wood, as is the case with merely painted wood tanks.

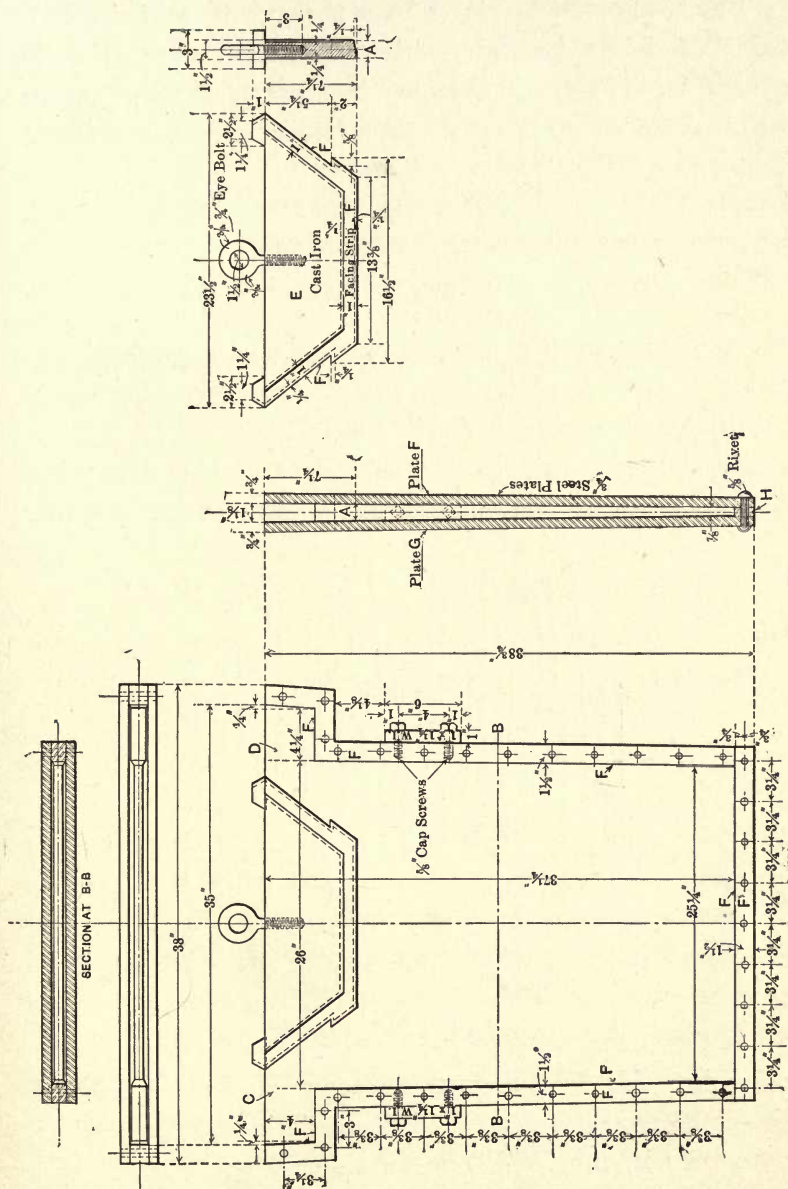
There are two styles of bus-bars in the refinery, as shown in Fig. 69. They and the cathode cross-bars are kept scrupulously polished so the contact losses are only from .01 to .05

volt for each contact, averaging about .02 volts or less. There are three sets of contacts to the tank, bus-bar to anode, cathode to cathode cross-bar, and cathode cross-bar to bus-bar. Small iron clips are driven on the cathode and cathode bar, after the tank has been loaded, to ensure good contact throughout the tank. The clips are as shown in Fig. 70.

The anodes are cast in closed upright molds, ten at a time, similar to Fig. 71, which shows some new molds that have been ordered differing from those at present in use only in that they are to be made of steel instead of cast iron, the taper allowed for withdrawing the lead is to be less, and the size of the anode head is reduced. Mr. Miller has applied for a United States patent on this mold.

The main body of the mold only is to be made of steel, and the wedge is to be of cast iron. The present molds operate very well, and when the anodes are lifted by power three or five at a time, instead of by a chain-block as at present, the cost for labor per ton cast is not expected to exceed 20 cents, though at present it is higher, namely about 27 or 28 cents per ton, with wages of 35 cents per hour. The molds are placed upright in a wood box arranged with a set of water sprays to cool each mold. The lead is pumped from the kettle into the mold with a centrifugal pump, which was originally a water-pump. This pump remains at the bottom of the kettle continuously and has already been in use for a long time with no repairs or cleaning. It is driven by a 3-H.P. motor through a belt and gearing. See Plate 10.

The anodes weigh 370 to 380 pounds each. At present the percentage of scrap returned to be remelted is about 20 but this will be considerably reduced with the new molds, which will make smaller lugs.





The anodes are lifted by man power with a chain-block and stacked in a vertical position, with the same spacing as is used in the depositing-tanks, in cars holding ten anodes each. There are 40 of these cars at the plant. Before lifting

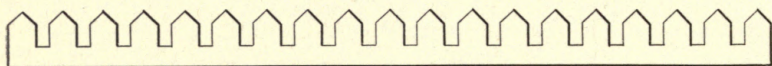


FIG. 72.

into the tanks two cars are run together, and a spacing-board protected from wear by sheet iron is placed over the top to give the exact spacing. (Figs. 72 and 73.)

The anodes remain in the tanks eight or nine days when the full current is passing, giving two crops of cathodes four

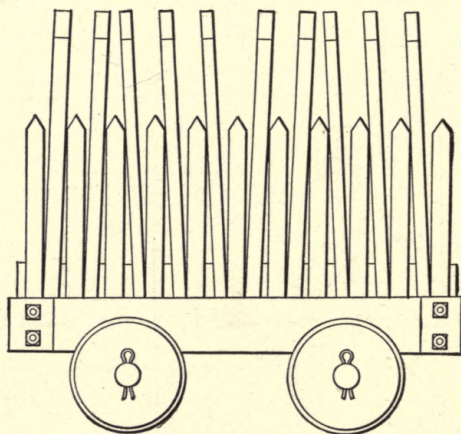


FIG. 73.

to five days old. The production of only one crop of cathodes per set of anodes has been tried and it is contemplated to go back to it, from which one would conclude that the cost of refining was about the same either way.

The anode scrap with most of the slime still adherent is lifted by the crane, a portable tray (Fig. 74) is hung underneath the load by the "crane chasers," when the crane carries the whole to one of the large washing tanks, where it is deposited, while the scrap is handled therefrom individually on a chain-block by the men who clean scrap. This requires three men on one shift. The cleaned scrap is thrown on a small flat car and wheeled to the bullion-kettle and dumped in.

The cathodes are made on the sloping table, one man

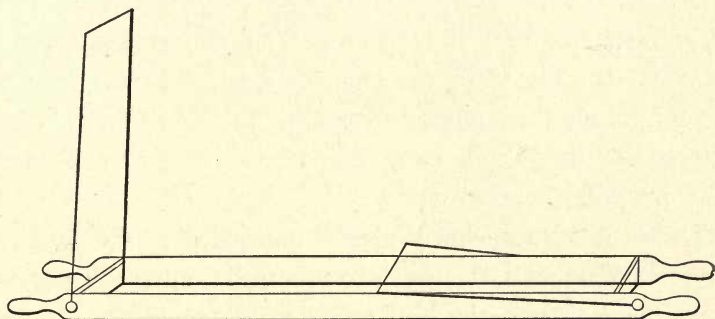


FIG. 74.

making 400 sheets in eight hours, while the night watchman makes 200 to 250 sheets during the night while not engaged in his other duties. The sheets are taken on small flat cars to the hanging room, where they are placed on a table, flattened out, wrapped around the cathode cross-bars two or three times, the men using a stick to bring the lead close to the copper. They are then hung, 21 to the load, on small cars provided with convenient supports. To place them in the tanks they are wheeled through the aisle to a position opposite the tank, and a man stands over the tank, reaches over

to the car and lifts the sheets one at a time into the tank. The entire operation of charging a tank with cathodes, fixing the spacing and contacts, and wheeling the car to the tank and away again requires about fifteen minutes for one man. For lifting cathodes to and from the tank, two styles of lifting racks are used. There are several of each at the refinery. The cathode lifting rack, which is the most complicated, may be seen in Plate 11.

The finished cathodes are lifted by the crane, the same pan being placed underneath as before, when the load goes to a washing tank where it is deposited and any slime wiped off and the plates splashed to get off the strong solution. They are then placed by the crane on a portable rack near the melting pot, and are pushed over into the pot by hand, which only takes a minute or two, the cathode cross-bars of course being previously pulled out.

The cathodes are slowly melted down during the day, and on the evening shift the pots are skimmed, and the centrifugal pumps lowered into the lead and the lead molded. The lead launder is about 22 feet long and there are some 160 molds in the circle. A crew of four men can mold about 20 tons per hour, but they do not work as fast as this, as the two men who wheel the lead to the box-cars and pile it in them could not keep up, so that about 15 tons per hour is the usual speed. The six men do all the work, including firing, skimming, and loading.

The use of a centrifugal pump for raising lead gives the best satisfaction, and is to be preferred to any of the other methods. This idea originated with Mr. Miller, of the Trail Company. A two-inch pump is about the right size, and costs about \$13.00 at Seneca Falls, N. Y. It is necessary to find



the right speed at which to run the pump before it can be worked satisfactorily.

The slime is collected from the electrolytic tanks, after siphoning off the clear solution, by a man who gets into the tank with a pail and shovel, and raises the slime by hand into a copper tank about 15 by 30 inches which runs on a small car between the tanks. A piece of oilcloth is hung over the top of the tank and of the copper tank to keep from losing slime and getting the bus-bars dirty. No pains are taken to get the tank entirely clean, but on the contrary considerable slime is usually left in the tank. Quite a little slime is also collected from the large washing tanks, a hand-pump being used to raise the slime into the copper-tank cars. There are six of these cars at the plant, and two men are employed cleaning tanks and taking the slime to the slime washing tanks. The slime cars are hoisted on an elevator and run on rails over the slime washing tanks. A plug at the bottom of the tank cars is raised with a copper wire, when the slime drops through a screen into the washing tanks. Frequently a hose is turned into the tank car to wash out the heavy slime. There are four of these washing tanks, which are of wood, side by side, each about 42 inches wide, 8 feet long, and 5 feet deep. The decantation method of washing is in use, and the results are reported on a slip like that shown below. The slime is stirred once by a paddle, and steam blown in. After settling, the clear solution is siphoned off into one of three launders according to destination, the strong solution being returned to the electrolytic tanks, that of medium strength going to the evaporators, while the weakest is used for washwater. The solution with which the slime is saturated is finally reduced to about 2° Beaumé. The slime is

finally run out through a large hose fastened into one end of the tank, and ordinarily held up against the end, into several wood suction-filters.

TRAIL REFINERY.

SLIMES WASHING.

Date, July 11, 1907.

TANK No. 4			TANK No. 5		
Wash No.	Beaumé.	Destination.	Wash No.	Beaumé.	Destination.
Slimes			Slimes		
Water...	30	Pump	Water...	40	Pump
1.....	20	"	1.....	30	"
2.....	10	Evaporator	2.....	20	"
3.....	6	"	3.....	10	Evaporator
4.....	2	Washing	4.....	6	"
5.....	0	"	5.....	2	Washing
6.....			6.....	0	"

TANK No. 1			TANK No.		
Wash No.	Beaumé.	Destination.	Wash No.	Beaumé.	Destination.
Slimes			Slimes		
Water...	40	Pump	Water...	30	Pump
1.....	22	"	1.....	20	"
2.....	20	"	2.....	10	Evaporator
3.....	10	Evaporator	3.....	5	Washing
4.....	5	"	4.....	2	"
5.....			5.....	0	"
6.....			6.....		

REMARKS:

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Signature.....

The evaporation of the washwater is conducted in a wood tank about 8 feet square, in which is dropped a lead pipe through which steam is passed. The acid lost during the evaporation is three pounds  $\text{SiF}_6$  per ton lead refined.

**Slime treatment.**—Mr. Alexander McNab's method of treating slime is now used. The slime from the washing tanks is first sucked dry as possible on the suction-filters. The slime is then neutralized by stirring into it a little caustic soda, and transferred in about 600-lb. lots to one of six or eight large iron tanks about 3 feet wide, 8 feet long, and 4 to 5 feet deep. The tank is then nearly filled with the sodium sulphide solution as it runs from the antimony depositing tanks, and 25 lbs. of sulphur is added. It is stirred with a wood paddle once, and steam turned in, which is thereafter sufficient for the stirring. After about two hours' boiling the solution is settled and siphoned off, and the tank is again filled with sodium sulphide, sulphur being omitted this time. After boiling and settling again the clear solution is siphoned off and added to the same storage tank as the first lot. The slime is drained and treated further as will be described below.

The sodium sulphide extracts about 80% of the antimony and some arsenic, and converts a good part of the remaining metals into sulphides. Contrary to what would be expected, most of the arsenic remains in the slime until the final melting to doré bullion. The sulphide solution contains about 3.5% of antimony after the slime treatment, and varying quantities of sulphide, polysulphide, and thiosulphate. The solution is collected in suitable storage tanks, and run through a series of antimony depositing tanks of iron, with sheet steel cathodes and lead anodes. The anodes are the



same kind of sheets as are used in the lead depositing tanks for cathodes. There are ten of these tanks in two cascades of five each. They have each about 240 square feet of anode and 240 square feet of cathode surface, and can take a current of 3000 to 3500 amperes with a potential when working without polarization of about 1.5 volts each. A temperature of about 60° C. is used as giving the highest efficiency. The iron tank is itself connected as cathode. The lead anodes remain in working condition about ten days and are then renewed. The current efficiency is about 45%. No diaphragms are used. The solution running out of the last tanks contains about 1% antimony, and is returned to be used for extracting antimony from fresh slime. The operation of the tanks is entrusted to three men, one on each shift. When the antimony deposit of the cathodes gets about one-eighth inch thick, they are taken out one by one and the antimony knocked off by hammering. Each tank has about 20 cathodes about 2 feet wide and 3 feet deep. The sodium sulphide is changed by electrolysis to thiosulphate, which means a heavy loss of sodium sulphide. Attempts will be made to crystallize out the thiosulphate of sodium and reconvert it to sulphide by reduction with carbon at a red heat. This part of the plant is running at a loss at the present time, partly on account of a drop in the price of antimony, but mainly because the percentage of antimony in the bullion has recently dropped to less than one-tenth of one per cent, and the percentage extracted by the sulphide solution is much less when there is only a little antimony present. The antimony deposited contains a little arsenic, which can be removed if too much is present by melting under an alkaline slag.

One of the principal items of cost of the process is the heavy cost for sodium sulphide, which is quite expensive when delivered at Trail. Mr. McNab mentioned that the loss of  $\text{Na}_2\text{S}$  would be about 30 lbs. or less per ton of Trail bullion, without recovery or regeneration of the solution.

To use this process continuously it would be very necessary to have extremely good ventilation where the sulphide solution is stored and handled, for the gases given off are injurious.

The treated slime has run as high as 27% arsenic and 4 to 10% antimony, while the raw slime contains perhaps 10% arsenic.

The deposited antimony contains some gold and silver.

The slime is next dried in a large iron pan placed over the roasting-furnace flue, with a hole in the bottom, so that it can be dropped directly into the furnace. The roasting-furnace is of the muffle type, and is hand raked. Its length for the hearth appears to be about 20 feet and width about 7 feet. The slime is calcined at a very low heat for the production of the oxides, arsenates, antimonates, and sulphides of lead, silver, and copper, and is finally raked into a large steel bucket suspended by a chain block from an overhead runway. The roasted slime is leached with sulphuric acid and water, taking out most of the copper and one-third to one-tenth of the silver, which is precipitated by metallic copper. The copper sulphate is crystallized out and sold.

The residue is melted in a magnesia-line reverberatory furnace, using Crow's Nest Pass coal, with silica as a flux to slag off the lead. This is a tedious operation, as the lead sulphate and silica do not react readily. They are going to try

my suggestion to put some old slag in each charge to help the melting. The parting is done by the sulphuric acid method, and the copper sulphate is crystallized for the market. They will probably try another suggestion to heat the roasted slime with sulphuric acid direct to make nearly all the silver soluble, which should save melting the silver twice.

There is a fluosilicic-acid plant which distils a mixture of fluorspar, silica, and sulphuric acid in iron pans about 8 feet diameter. The acid fumes are condensed in wood towers about 1 foot square and perhaps 20 feet high, through which a spray of water is dropped. The fumes pass up and down through a series of some six towers. The plant was not in operation on account of shortage of sulphuric acid, at the time of my visit. Excellent results are claimed for this plant.

**Labor required.**—The tank-room labor is subdivided as follows: In addition to the general foreman, there are three shifts of three men each who inspect the tanks for short circuits, clean bars, empty and fill tanks with solution, put on and take off clips, and clean cathodes. Two men are employed putting cathodes into the depositing tanks. Three men clean the anode scrap; two men clean tanks; one man runs the crane; one man attends to the changing of the electric connections and the siphons; three men hang sheets; two boys clean cathode cross-bars; one man makes sheets; one man for night watchman who also makes some sheets; one man on the day shift and one man on the evening shift are employed in washing slime free from lead-depositing electrolyte, and two men follow the crane, making one foreman and twenty-nine men in all. The wages are 34.5 cents per hour and the



men get out 45 to 50 tons at the present time in about 6.5 hours. I am informed both by the superintendent and the foreman that the same crew could handle the full 80 tons in eight hours, with two or three additional men. The reason for this is that there is not sufficient work for the men at present, and the men are probably allowed to waste a good deal of time, as they are paid by the hour, and labor is so scarce that they would leave if they only got five hours work a day.

With a production of 50 tons per day the labor cost is evidently about \$1.40 per ton at present, and with 80 tons produced per day, it would be about \$1.17 per ton. With labor at 25 cents per hour it would evidently be for 80 tons per day about \$0.85 per ton. Eventually the plant will probably have an anode-wiping rig that will handle a tank-load of scrap at a time, and if the plant had more slime washing tanks, or if they were larger, one man could easily do the work that now takes two men, which would reduce the cost per ton at Trail on the 80-ton scale by about 10 cents.

The labor loading and unloading lead and bullion and firing and melting takes, in addition to the general foreman, six men casting anodes (divided into two shifts) and six men on one shift casting and loading lead, and five men unloading bullion and shifting anodes, while one man fires the pots and dumps cathodes in the daytime. This includes the sampling of the bullion and the remelting of the anode scrap and skimming the pots. This force is fully employed to handle 50 tons on an eight-hour shift. The wages are the same as for the tank-room force, so the labor cost with the present arrangement of plant is evidently about \$1.00 per ton refined, including loading and unloading, firing, sampling, and wheel-

ing lead and bullion about the refinery. Certain reductions in this item are planned. It should be remarked that the refinery has no electric or other power traction system for moving lead around, and there is a chance to make a saving there. Forty pounds of coal are consumed per ton of lead melted. The refinery will probably ultimately receive bullion in the form of anodes instead of pigs, which will save quite a little expense. The repair item is very small with the steel pots in use, which last for a very long time. There are employed at the refinery two carpenters and one machinist, for repairs and improvements. There are two 80-H.P. boilers which are fired by the same man who runs the electric generators, three in all for the three shifts.

In the slime plant there are employed one foreman; two men boiling slime with sodium-sulphide solution; three men on the antimony depositing tanks, who also take care of the lead fluosilicate-solution evaporators; two men drying and handling slime; three furnacemen on the roasting furnaces; and one man in the copper-sulphate crystallizing plant, twelve men altogether. I did not make any inquiry about the parting process and operation, as that is such a well-known process anyway.

The superintendent's assistant keeps the records of operation, shipments, etc.

At the time of my visit the electrolyte in the lead depositing tanks was rather weaker than usual owing to a scarcity of sulphuric acid for making fluosilicic acid, and contained about 5 gr. lead and 10 gr.  $\text{SiF}_6$  per 100 cc. I was informed that the greatest economy at Trail, after taking into consideration everything, as power, acid loss, etc., was reached with a solution containing about 12 gr.  $\text{SiF}_6$  per 100 c.c

It would be expected that at Trail, with expensive acid and not very expensive power, the greatest economy would be achieved by economizing in acid at the expense of some power. The acid loss for the preceeding two months had been 7 and 6 lbs. of  $\text{SiF}_6$  per ton lead respectively. Mr. Miller informed me that he thought it averaged about 8 lbs. when the plant was running full. The circulation is maintained at about 5 to 7 gallons of solution per minute for each tank. The current efficiency averages about 88%. The e.m.f. per tank is about 0.4 volts.

The daily report is made out on the form shown:

### TRAIL SMELTER

#### LEAD REFINERY REPORT.

May 31, 1907.

#### TANK ROOM.

Pig Lead Produced.....lbs.	Last 10 Days.....	465.36 tons
Pig Lead Produced this Month to Date.....		1527.51 tons
Pipe.....		34 tons

Electrolyte	{	Acid	9.2	10.1	Pct.	Average Amperes ..	3066.6	
		Lead	4.4	5.0	Pct.		Average Volts. ....	72.2
		Sp. Gr.	1.13	1.16			H.P. ....	296.5
		Temp.	34° C.				Time Running. ....	24 hours

#### First Crop.

#### Second Crop.

Tank Efficiency. ....	95.7	Last 10 Days	98.3	Last Month	86.3
Lead per K.W. Hour. ....	20.2	" 10 "	20.7	" "	" "

No. of Tanks Charged.	Weight Anodes.	Weight Cathodes.	Weight Scrap.	Pet. Scrap.
.....	.....	.....	.....	.....
Starting Sheets, Made No.	378	Day Shift	210	Night Shift



MELTING-ROOM.

Refined Lead Shipped	Lot No.	1116	967	Pigs	87,915	lbs.
	Lot No.	1117	435	Pigs	40,001	lbs.
			1402	Total	127,916	lbs.

Refined Lead on Hand			Pigs		lbs.
	Lead Pipe.				lbs.
	Cathodes.				lbs.
	Total.				lbs.

Bullion Received, Lot No.....Bars.....lbs.

Bullion on Hand, Trail.....Bars.....H. M. Bars.....

No. Anodes Made Night Shift, 150 Day Shift, 190 Total

REMARKS.....  
.....  
.....

N. B.—Lead produced does not include pipe or dross.

Plates 8 to 13 show interior and exterior views of the refinery.

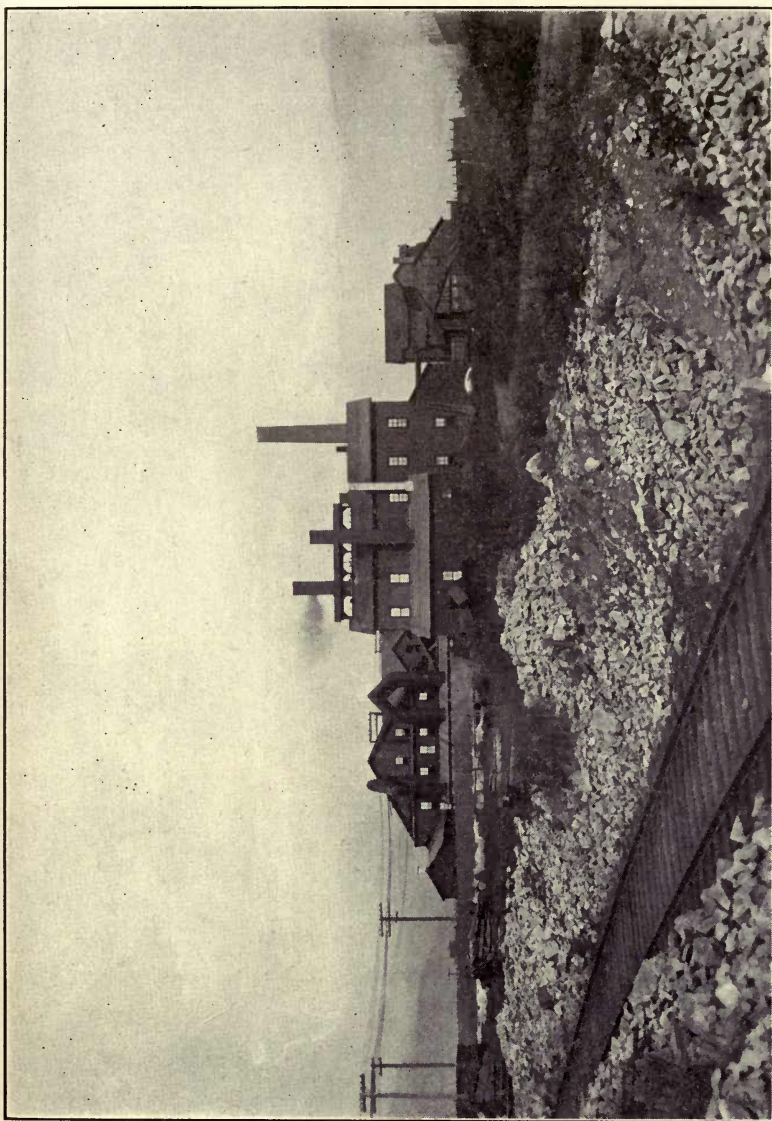


PLATE 8.

VIEW OF LEAD REFINERY.

Consolidated Mining and Smelting Co. of Canada, Ltd., Trail, B. C.







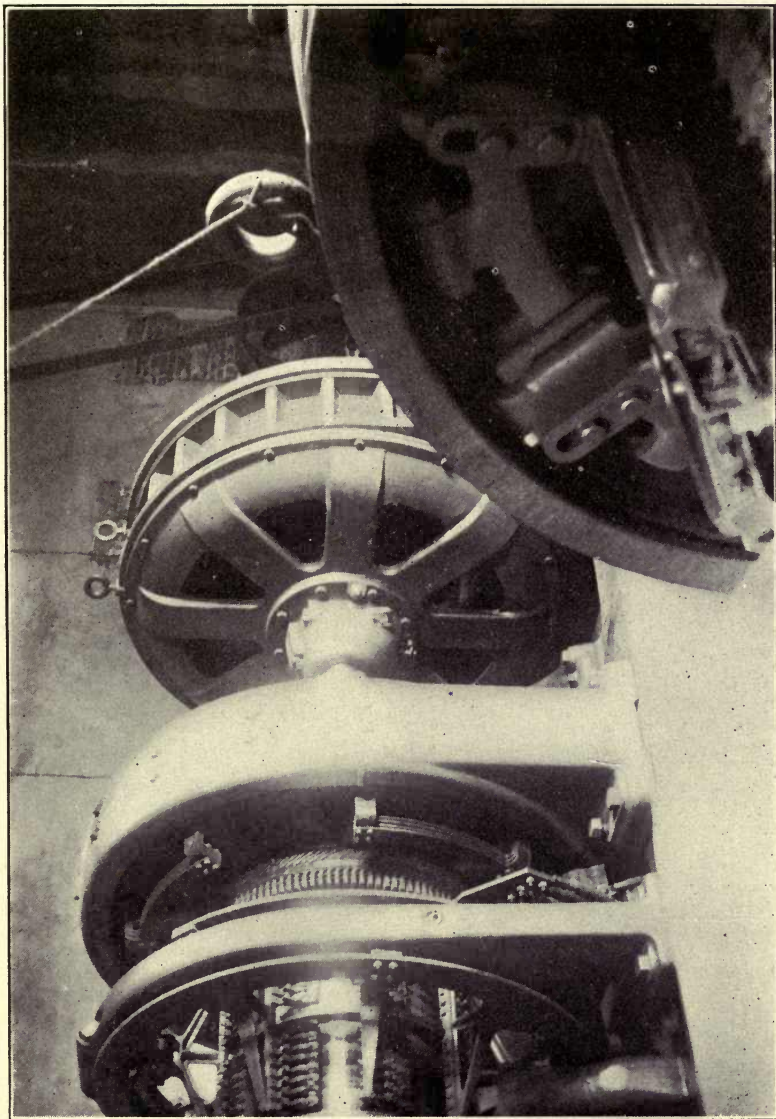


PLATE 9.

MOTOR-DRIVEN ELECTROLYTIC GENERATOR.

Consolidated Mining and Smelting Co. of Canada, Ltd., Trail, B. C





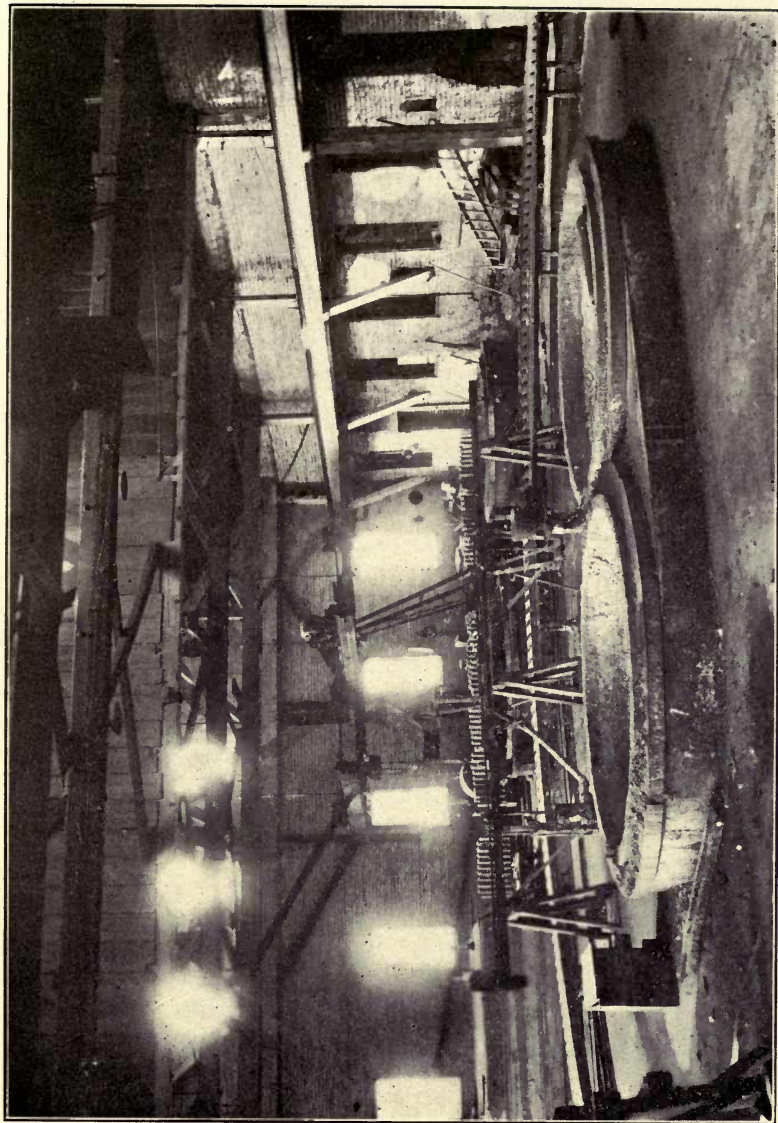


PLATE 10.

REFINED LEAD CASTING PLANT.

Consolidated Mining and Smelting Co. of Canada, Ltd., Trail, B. C.





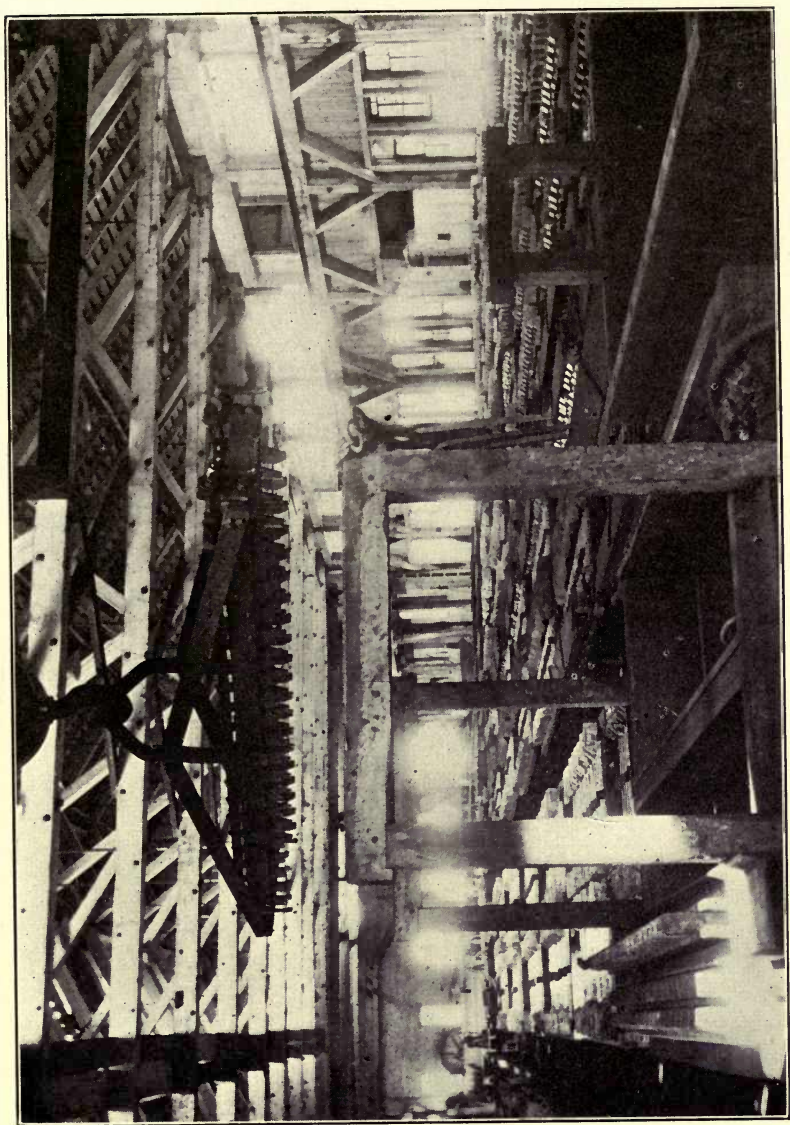


PLATE 11.

VIEW OF LEAD-DEPOSITING TANKS.

Consolidated Mining and Smelting Co. of Canada, Ltd., Trail, B. Co.







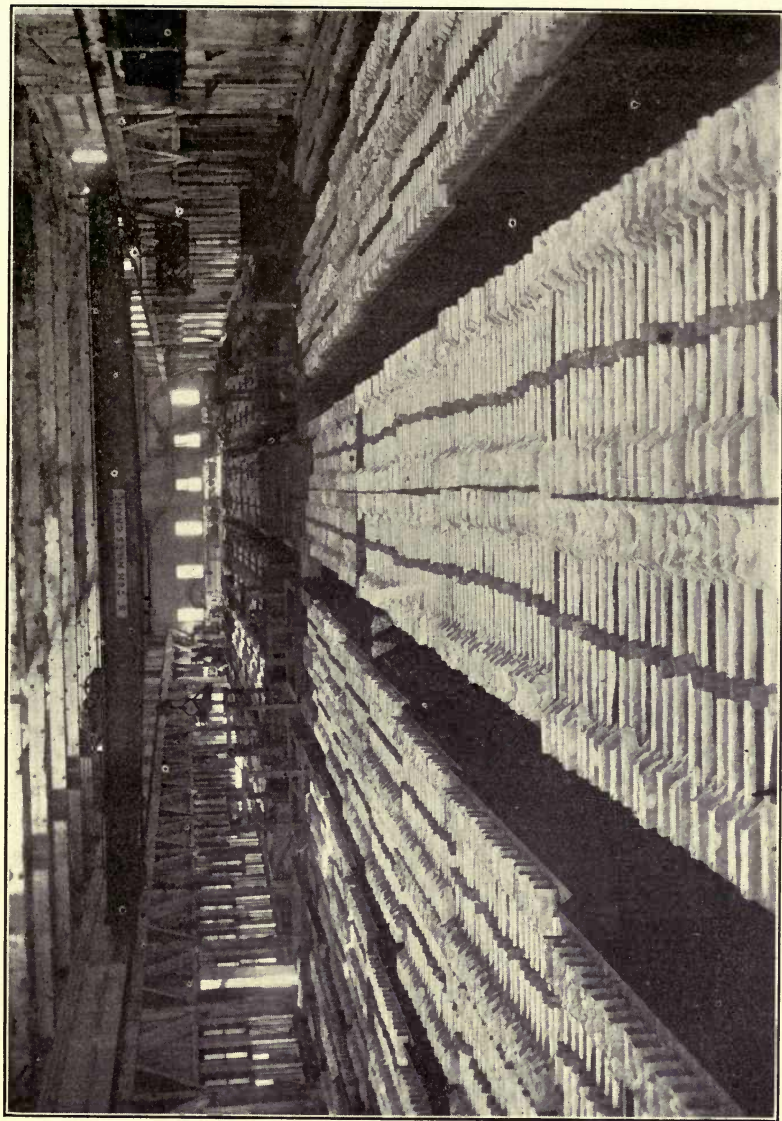


PLATE 12.

VIEW OF LEAD-DEPOSITING TANKS.

Consolidated Mining and Smelting Co. of Canada, Ltd., Trail, B. C.





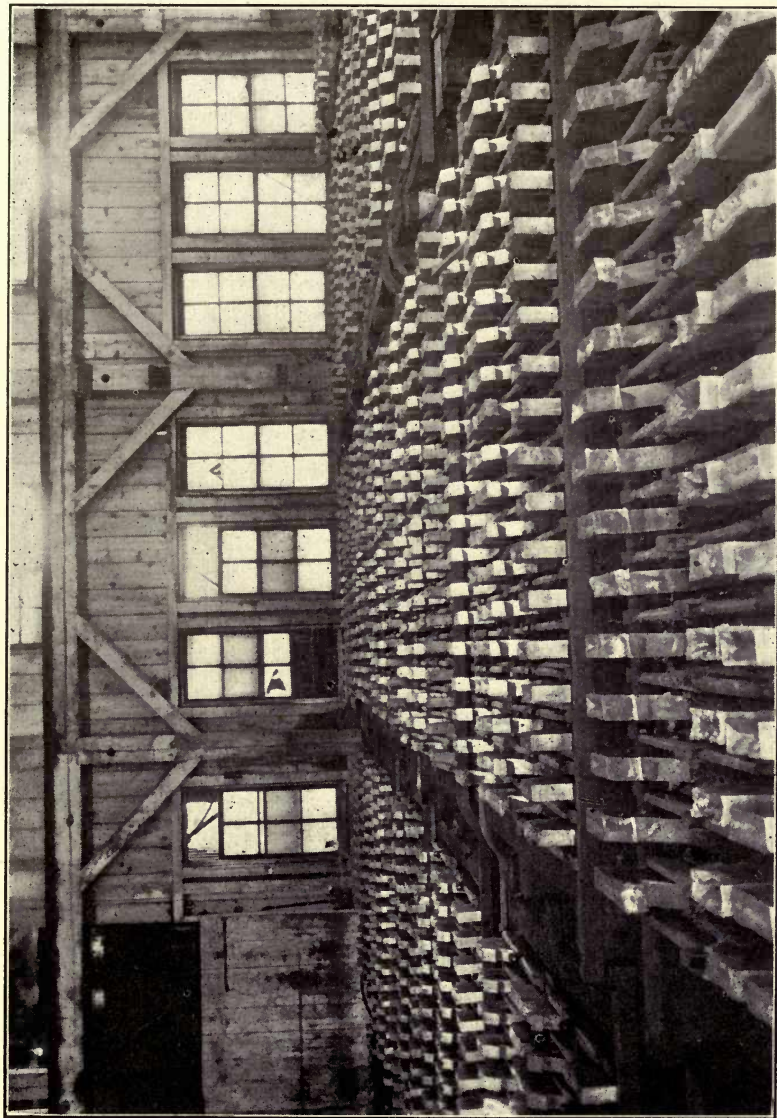


PLATE 13.

VIEW OF LEAD-DEPOSITING TANKS.

Consolidated Mining and Smelting Co. of Canada, Ltd., Trail, B. C.





## APPENDIX II.

### LEAD-REFINING PLANT OF THE UNITED STATES METALS REFINING COMPANY AT GRASSELLI, LAKE COUNTY, INDIANA.

THE principal buildings are an office building, tank and melting building, 72 feet by 360 feet for the depositing tanks and melting furnaces, a power plant at one end of the large building, and a hydrofluoric and fluosilicic acid building. The slime-washing machinery and evaporators are located in separate small buildings.

The power plant has two boilers, only one of which is required at a time. The fuel is local bituminous coal of fair quality. One cross-compound Nordberg engine drives a Crocker-Wheeler electrolytic generator, having its maximum efficiency at 60 volts and 4,500 amperes and capable of carrying considerable overload. The same engine drives by belting a small generator for power and lighting purposes. A smaller double-expansion Nordberg engine drives a Westinghouse 110-K.W., 110-volt, 1000-ampere dynamo which can be used for power and lighting purposes, and has very considerable reserve capacity. The power plant and the tank and melting plant are in handsome substantial brick buildings.

The tanks occupy the rear end of the large building near the power plant. The tank arrangement follows the Walker

system as used in copper refineries, but the number of tanks per block is four only instead of the large number used for copper.

Each tank takes 26 anodes (for size of tanks, etc., see page 214) and 27 cathodes of sheet lead weighing about 18 lbs. each. The cathodes are cast of the form shown in Fig. 57, and the sheets are hung over the cathode-bars, which are of copper about  $\frac{3}{8} \times 1\frac{1}{4}$  inches in cross-section, on a special table provided for the purpose. A hole is punched through the sheet and the overlapping strips, and the burr produced hammered out, giving a satisfactory hold, and a double thickness of lead at the solution line, which latter is a help in that there is little or no chance of the solution cutting through the cathode at the surface, during the time the sheet remains in the tank.

The tanks are lined with an asphaltum mixture. Great care is required in getting a proper mixture; one that will not soften at the temperature of the electrolyte and will not crack in cold weather if the tanks are empty.

Electric motor-driven centrifugal pumps raise the solution from the pump-tanks beneath the level of the depositing-tanks to the feed-tanks at a level higher than the depositing-tanks, leaving the rest of the flow through the tanks to be accomplished by gravity. The solution circulates through two tanks only before it again flows down to the storage and pump tanks.

The tanks are supported on concrete piers, which are well asphalted. The ground under the tanks slopes to sumps and is also well asphalted.

Two electric travelling cranes, 72-foot span, capacity 10 tons, command the entire tank and melting space. One crane



could probably do all the work quite well if the other should be out of order.

Tapering tank bus-bars are used to save in copper. All electrodes are supported on small triangular copper rods fastened to the bus-bars on the outside of each block of tanks, while for the intermediate supports the triangular pieces suffice.

The bullion comes to the refinery already cast in anodes, from the United States Smelter near Salt Lake City. They are unloaded from the box-cars and sampled by punching, with the help of a chain block and a temporary track run into each car, at a labor cost of probably about 6 cents per ton. The anodes are 2 feet wide and 3 feet deep and weigh about 450 lbs. each.

There are two melting kettles at one end of the main building nearest the railroad track, one of which is used for melting refined lead and the other for making fresh anodes from the anode scrap. The pots are at quite an elevation above the floor, so that the lead may be siphoned out, though it is the intention to use a centrifugal pump as at Trail. The lead is molded in the usual manner and goes into the market marked "electrolytic." The bullion is molded into ten flat open molds, and removed with an air hoist running on an overhead track.

The washing of the cathodes is now done with a spray, though the method in use at Trail will probably be adopted, as it is perhaps a little quicker. The anode scrap with attached slime is hung by the tank-load in a tank of about the same size as the electrolytic tanks, and a gang of five men with scrubbing brushes attached to poles about six feet long, reach in between the anodes and wipe off the slime into the solution

or washwater in the tank. The crane then picks up the load, when it is washed with a spray of water and is then carried to the pot, and lowered part way in. When the crane travels off the side of the pot draws the cathodes off the lifting rack, and the cathodes fall in. The crane has two lifting ropes, one at each end of the lifting rack, otherwise this method would not be practicable.

The slime removed from the anode scrap, and that collected from the bottoms of the electrolytic tanks is piped to a separate building. Part is pumped into a large iron filter-press until the press is filled up, when an air blast is turned in to get as much of the strong solution out as possible. The slime is then washed with cold water, until the solution running out is reduced to 2° Beaume, when the air blast is again turned in to dry the slime. The rest of the slime is washed in two centrifugal machines with copper baskets. The slime is next dumped into iron drying pans heated by a fire (steam drying is too slow), and when the moisture is reduced from about 40% as it comes from the filtering machines to 10 or 20%, it is barrelled and shipped to the company's refining-plant at Chrome, N. J., for further treatment.

The strong solutions and washwaters from the filtering plant are probably returned to the electrolytic tanks, while the weaker are evaporated. The evaporation is partly carried out in wood tanks as at Trail, and also in a large circular tank of hard lead, the latter being decidedly the best.

The lead-depositing electrolyte at the time of my visit contained about 6 grams of lead and 9 gr. of  $\text{SiF}_6$  per 100 cc. The temperature was about 32° C. and the volts per tank about .45. The solution will undoubtedly be strengthened up later.

The acid-making plant is very complete. The fluorspar, slightly in excess, is mixed with not too strong sulphuric acid and distilled, and the hydrofluoric acid produced is saturated with silica in tanks with mechanical agitators. The results are excellent, and the building is usually free from acid fumes.

Plates 14, 15, and 16 are views of the works.





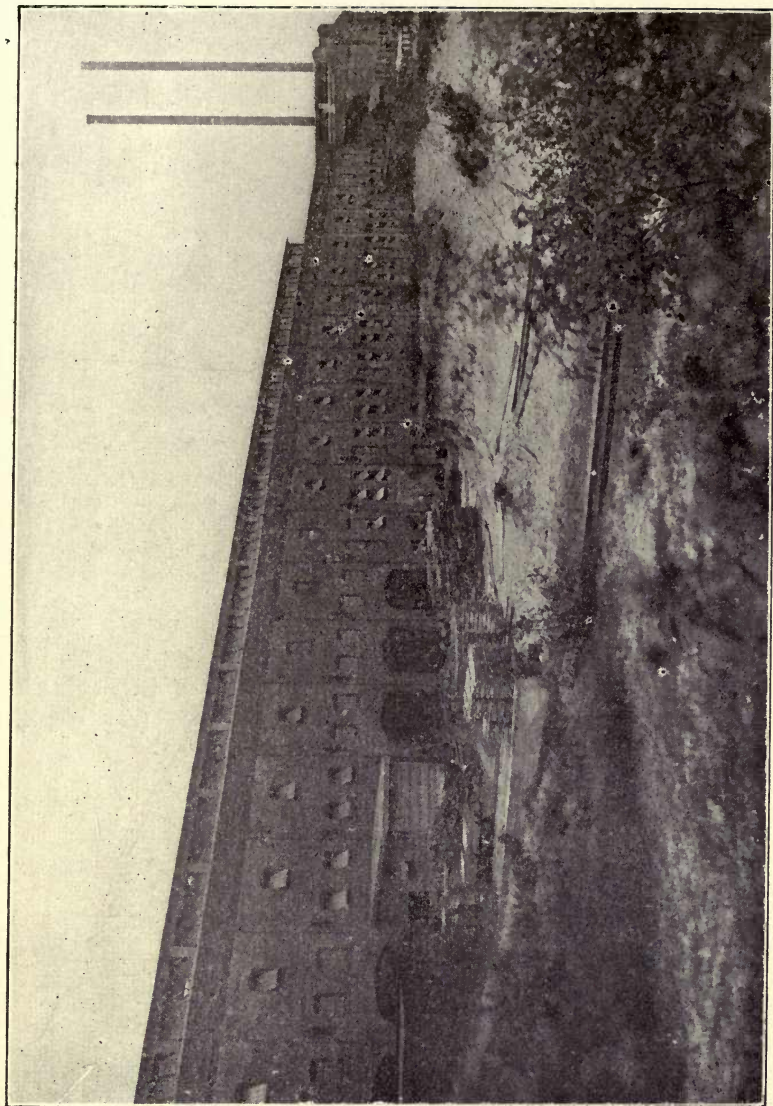


PLATE 14

TANK AND POWER BUILDINGS.  
United States Metals Refining Co., Grasselli, Ind.







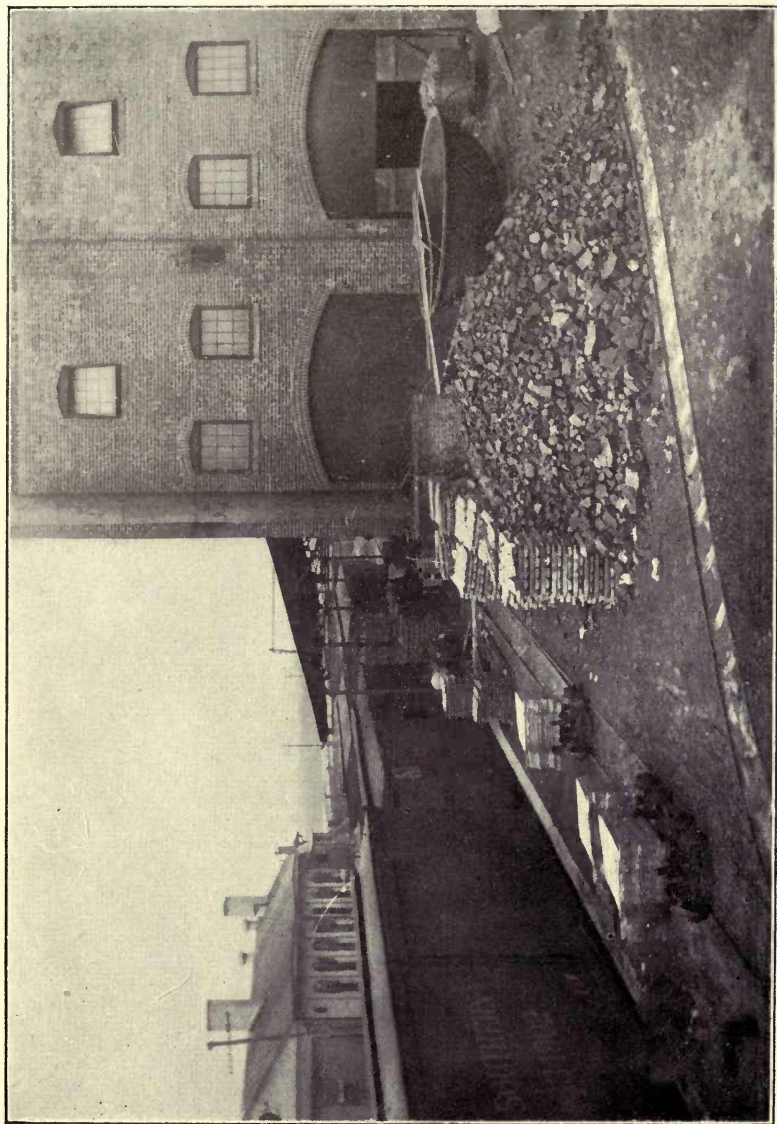


PLATE 15.

SHIPPING PLATFORM.

United States Metals Refining Co., Grasselli, Ind.





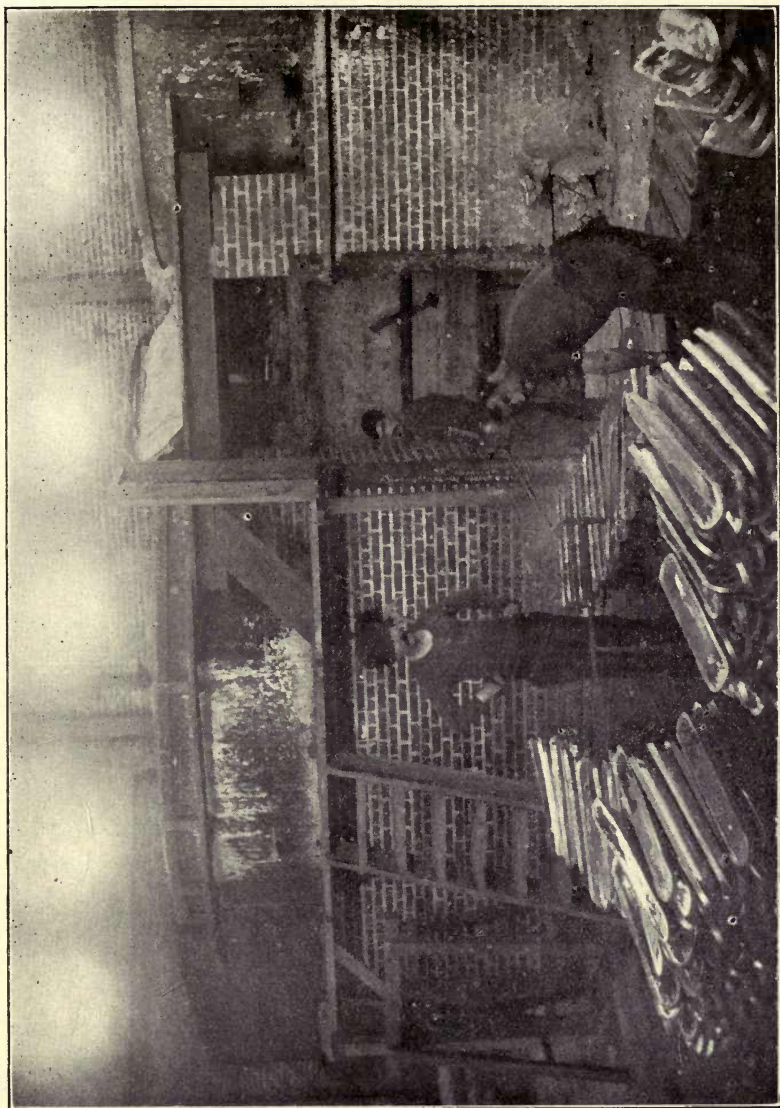


PLATE 16.

LEAD KETTLES.

United States Metals Refining Co., Grasselli, Ind.





### APPENDIX III.

#### TREATMENT OF LEAD REFINERY SLIME WITH SOLUTION OF FERRIC FLUOSILICATE AND HYDROFLUORIC ACID.

THE treatment of lead refinery slime is on a fairly satisfactory basis, by methods discussed in Chapter II, but in the endeavor to carry the electrolytic treatment to greater perfection I made experiments in my laboratory, which I shall describe below.

The experimental operation was on a scale corresponding to the treatment of the slime from one ton of lead bullion per day. The experimental plant was run continually twenty-four hours each day in charge of two shifts, while daily analyses of important products were made, to follow the operation as closely as possible.

There were so many difficulties to contend with, principally with the apparatus, that after running about a week, I was obliged to shut down and make changes. After starting up again the plant was operated continuously for two weeks, until the supply of slime on hand was practically used up.

During the middle of the second run the supply of lead electrodes was used up, and the operating force was too busy to make more, so that it was a case of shutting down and beginning over again, or changing. The deposition of the separate metals was not being done well, and it seemed impossible

to do it, at least with the arrangement of plant. Partly under the force of necessity, I introduced a change in the process at this time, that turned out in a very gratifying way.

The scale of operation and the desire to operate the plant continuously afforded a better test of what could be done on a commercial scale, than smaller laboratory tests could have possibly given.

The process used was referred to in Chapter II, page 92, and is similar in some respects to processes mentioned on pages 119-123 and 134-137. In a general way the process consists in attacking the fresh unoxidized wet slime with a solution of ferric fluosilicate and hydrofluoric acid which removes over 99% of the arsenic and copper, 90% or more of the antimony, and nearly 90% of the lead. Originally it was intended to remove from the resulting solution, first the copper as cathode metal, while antimony anodes dissolved, thus substituting antimony for copper. Next the antimony was to be deposited using lead anodes which dissolve, so that lead takes the place of antimony in the solution. After this the arsenic was to be plated out as a lead-arsenic alloy, while lead anodes were also used in this case, thus substituting lead for arsenic. The solution now containing only lead and ferrous fluosilicates was to be electrolyzed for metallic lead and ferric fluosilicate, the latter to be used over again in the same way as before. Of course the different electrolytic steps were to be performed in separate sets of tanks through which the solution flowed in series.

Later, the electrolytic deposition of copper, antimony, and lead-arsenic was given up and the metals cemented out in layers of different composition by causing the solution to flow through the lead product obtained in the ferric-iron producing



tank. This gave a separation, although the antimony and arsenic were recovered together.

The use of hydrofluoric acid in the solution is important, because without it only a little antimony could be dissolved. If hydrofluoric acid only was used lead could not be extracted. By the addition of hydrofluoric acid to the solution within certain limits, the extraction of the antimony may be secured, without spoiling the lead extraction.

The ferric fluosilicate-hydrofluoric acid seems to me to be probably the best of all wet slime processes, because it offers these advantages: A minimum of electrolysis to produce the desired products; recovery of any lead refining solution or any fluorine left in the slime by incomplete washing, or decomposition of the lead depositing electrolyte; treatment of wet, raw, and imperfectly washed slime; simplicity; no chance to lose valuable metals; elimination of arsenic from the slime-treating solution; and recovery of the arsenic. Very few of the slime processes have any of these advantages.

Experiments were made to find a suitable electrolytic diaphragm capable of withstanding solutions containing hydrofluoric acid. With asbestos and earthenware impossible, it is not an easy matter to produce a diaphragm. Quite satisfactory tests were obtained with carbon buttons, prepared by mixing powdered charcoal with asphaltum varnish and stamping into buttons  $1\frac{1}{4}$  inches diameter and  $\frac{3}{16}$  inches thick, which were dried and baked gently. Using soft charcoal and baking below a red heat the product was electrically non-conductive, and after removing air under an air-pump, or boiling in a solution of sodium nitrate, gave a fair electrolytic conductivity.

Preliminary tests were made on two lots of lead slime.

Lot 1 had been partially dried in the usual course of treatment and was pretty well oxidized. Lot 2 had been merely filter pressed, and was practically non-oxidized. The latter kind only is suitable for the ferric fluosilicate-hydrofluoric acid process. The analyses are given in Table 121. The last analysis given for Lot 2 is the most accurate.

TABLE 121.

	Lot 1.	Lot. 2.	
Moisture .....	20 %	47.75%	
Antimony on dry residue.....	33.75%	39.22%	
Copper on dry residue .....	1.45%	2.25%	2.45%
Arsenic .....	12.60%	14.10%	16.00%
Silver .....	12.08%	16.24%	17.20%
Bismuth .....	1.60%		2.60%
Tellurium .....			1.30%
Selenium .....			trace
Iron .....	0.50%		
Lead .....	12.06%	9.88%	11.9 %
Fusol .....	16.00%		

The amount of ferric iron required for a given slime can be calculated from its composition, if the slime is unoxidized, or determined experimentally. The method of testing the iron-reducing power consists in boiling with an excess of ferric-sulphate and boiling the filtrate with metallic copper until all ferric iron is reduced. Multiplying the amount of copper dissolved by 1.76 and subtracting the result from the amount of ferric iron used gives the iron reduction figure. Of Lot 2, 100 grams as dry slime reduced 94.5 grams of ferric iron, which shows practically no air oxidation to have taken place. Of Lot 1, 100 grams as dry slime reduces 13.8 grams ferric iron, showing approximately 85% air oxidation. This is about the usual figure for soft slime, dried in air.

A test on 100 grams Lot 1 with ferric fluosilicate and hydro-

fluoric acid gave a 25-gram residue, containing Fe 3.5%, Cu none, Sb 18.5%, Bi 3.45%, Pb 9.35%.

TABLE 122.

	In Original Slime	In Residue.	Fer Cent. Dissolved.
Antimony .....	27 grams	4.62 grams	82.9%
Copper .....	1.16 grams	none	100.0
Arsenic .....	10.1		
Lead .....	10.1	2.34	76.5
Bismuth .....	1.28	0.86	37.8

Six hundred and fifty grams of Lot 1 (520 grams dry weight), leached with a fluosilicate-fluoride solution containing 42 grams ferric iron gave a 159-gram residue containing 39.8% silver, 10.5% antimony, no copper, 24% lead, no arsenic, 3.41% bismuth. This shows an extraction of 90% of the antimony; all copper and arsenic; 42% of the lead, and 40% of the bismuth.

The poor extraction of lead was due to the solution containing too much HF, so that lead fluoride was formed and remained undissolved. The percentage of bismuth extracted is not of great importance, as the process recovers both undissolved and dissolved bismuth. The solubility of bismuth in these solutions was approximately 1 gram per liter.

No further preliminary tests were thought necessary on Lot 2.

The apparatus to be used consisted of a series of tanks. In the first the solution from the slime is electrolyzed with a low current density of about five amperes per square foot, using copper cathodes and antimony anodes. The antimony dissolves at the anodes while copper and presumably bismuth deposit. The solution is supposed to flow from the tanks



practically free from copper and bismuth. The next series of tanks was much larger and contained lead anodes and copper cathodes; lead dissolving and antimony depositing, with a current density of about 12 amperes per square foot, which was found later to be decidedly too high, so more tanks were used and the current density reduced to 7 amperes. Leaving these tanks, the solution containing a little antimony passes through another somewhat smaller set, having lead anodes and cathodes. In the first of this set lead and antimony with some arsenic, and later lead and arsenic, and finally nearly pure lead deposit, or at least were expected to. The anodes in the antimony-depositing tanks contained about 0.6% antimony, and those in the arsenic-depositing tanks were of practically pure lead. The dimensions of these tanks are given in Table 123.

TABLE 123.

	No.	Length, Inches.	Depth, Inches.	Breadth, Inches.	Cathodes, Inches.	Anodes, Inches.
Copper tanks . . . . .	6	6	8	7	6 × 6	6 × 7
Antimony tanks . . . .	3	11	17	14	13½ × 16	10 × 13½
Arsenic tanks . . . . .	3	10	16	12	10½ × 12½	10 × 13½

All tanks were fitted with independent agitators capable of maintaining a good circulation, which is very necessary with this process, because the solutions, except in the ferric iron tank, are very dilute with respect to the metals being deposited.

The diaphragms for the ferric-iron tank were prepared by stamping a charcoal and asphaltum mixture into buttons, 1½ inches in diameter, and about ⅜-inch thick, drying and baking below a red heat. About 2150 of these were inserted and made fast with thick asphaltum varnish in holes bored in

the sides of five wooden boxes, which were to form the anolyte compartments. These boxes were made of  $\frac{3}{4}$ -inch wood, and were 3 inches wide by  $30\frac{1}{2}$  inches long by 22 inches deep inside. Before inserting the carbon buttons they were boiled in sodium nitrate solution to drive out the air and wet the buttons, so that they would finally become wetted through when electrolyte was added to the tank. The buttons also expanded a little by this treatment. The space occupied by the buttons on each side of each box was about  $21\frac{1}{2}$  inches by  $29\frac{1}{2}$  inches. As 215 buttons had an area of 264 square inches, the current density in the buttons averages about 2.5 times higher than the anode and cathode current density and approximated 20 amperes per square foot.

Five of the anolyte boxes were spaced with distance frames, about  $3\frac{1}{4}$  inches apart in the clear between the boxes, in an asphalted wooden tank with an internal length of 42 inches, width 35 inches, and depth 24 inches. The whole was driven tightly together with wedges inside the tanks at one end, while the tank was securely braced outside to prevent its being strained by the pressure developed by the wedges.

The anodes consisted of five sets of Acheson graphite rods, one inch in diameter and 24 inches long, cast in lead at the top and carried by reciprocating beams at the sides of the tank. The total motion was  $\frac{3}{4}$  inch. There were 19 anodes to the frame, spaced with  $1\frac{1}{2}$  inches centres. The actual anode surface was about 4% greater than would be presented by a plane of the same overall measurements. The total anode area exposed was approximately 41.5 square feet. The six cathodes were of sheet lead  $21 \times 28$  inches with an exposed total area of about 41 square feet. With a current of 330 amperes, this corresponds to a current density of about 8 amperes per square

foot. Provision was made to keep all the catholyte and anolyte in good circulation through the various respective compartments. The circulating apparatus adopted did not work well at all, unfortunately, with the result that the solution in some of the anolyte boxes contained no remaining ferrous iron for a large part of the time, and the anodes after the runs were over were found to be considerably attacked in those places, although in other places, even where as much current was used, there was no evidence of corrosion.

The total cubic capacity of the electrolytic tanks, taking account of space occupied by electrodes and diaphragms, was about 25 cubic feet, while, when all tanks but the iron tank were cut out, the capacity approximated 15 cubic feet.

The solution was made up originally by first dissolving scrap wrought iron in fluosilicic acid, and then treating 70 lbs. of oxidized slime of Lot 1 with a part of the solution. The solutions were then mixed together for the tanks and contained 12.4 grams  $\text{SiF}_6$ , 0.1 gram copper, 2.55 grams iron, 1 to 2 grams HF, and 0.86 grams antimony per 100 c.c.

The treatment of the slime of Lot 1 by  $\text{SiF}_6$  and HF did not give as high an extraction as was expected from the tests made previously. A possible explanation is that the top of the barrel from which the slime was taken, differed in oxidation from the middle plane from which the sample was taken. A content of 2% or more of antimony was desired and had been expected.

The total amount of the solution used was about 900 liters.

The slime treatment so far was not successful, but the solution was most easily prepared in that way, and that was really the reason this particular method was used.



The solution was fed first to the copper-depositing tanks, and the others were gradually brought into action as they filled up.

The electrical conditions were about as follows, Table 124:

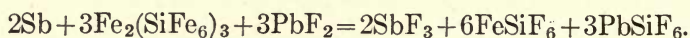
TABLE 124.

	Average Volts.	Average Current Density.
Copper tanks,	0.17	5 amps. per sq. ft.
Antimony tanks, 0.45, normally rose however to 2 volts at times,		7.4 " " " "
Arsenic tanks, 0.45, normally rose however to 2 volts at times,		1.7 " " " "

The antimony anodes in the copper tanks dissolved regularly and evenly. The lead anodes in the antimony tanks dissolved without difficulty, but lead fluoride formed during the first run in patches on the surface, and collected as a white mud in the bottoms of the tanks. The lead anodes in the arsenic tanks of practically pure lead did not dissolve well at first. The surface was quite rapidly covered with an insulating layer containing lead fluoride. These were then replaced with anodes containing about 2% of antimony, with the idea that the anode slime of antimony would act as a diaphragm and keep the HF in the solution away from the anode surface. The anodes dissolved better thereafter. The explanation is, that the current is principally carried by the  $\text{SiF}_6$  ion, the formation of lead fluoride being largely a secondary reaction between the  $\text{PbSiF}_6$  formed, and the HF.

The formation of lead fluoride in the tanks is not really necessary in the process, and did not occur afterward, but in the first part of the run the solution contained too much HF, and quite a little white lead had to be added to remove the excess.

The lead fluoride could be worked up by adding it to a batch of slime, when a reaction occurs as follows:



The copper tanks took altogether 6 to 16 amperes, arranged in two series, or 3 to 8 amperes per tank, with a current density of 3 to 8 amperes per square foot, and voltage of 0.2 to 0.24 with 6 amperes per square foot.

The antimony-depositing tanks took 60 to 150 amperes for the three tanks, or a current density of about 5 to 13 amperes per square foot, with normal voltage of 0.25 to 0.6. The deposited metal was of various kinds, and no pure antimony was produced. The voltage rose much higher at times, and probably oxidized some antimony to the irreducible  $\text{SbF}$ .

The "arsenic" tanks were operated with 10 to 100 amperes, averaging about 30, or a current density of 1 to 10 amperes per square foot. The voltage ranged from 0.5 to 1.5.

The large ferric-iron producing-tank had an extremely high resistance at first, until the solution had penetrated the pores of the carbon. At the end of the run the temperature had risen to  $36^\circ \text{C}$ . and the current rose to 335 amperes, with 2.5 volts.

No difficulty was experienced with polarization at the anodes, provided they were kept moving back and forth by the mechanism provided therefor. Otherwise the tank would polarize in a minute or two, and the voltage would show an increase of from 0.6 to 0.8 volts. The counter electromotive force of the cell determined by opening the circuit and reading the voltmeter was about 1 volt. No difficulty with silica depositing on the anodes and causing polarization and gassing was experienced with this process as with the ferric-sulphate

process, and this could not very well happen, because the solution contained free hydrofluoric acid, which would, of course, keep silica in solution.

Most trouble was caused by the carbon buttons loosening and dropping out in the tank. Part at least of this trouble was caused by faulty setting of the buttons. Some had been put in without any cementing material at all. The leaking holes were located and corked up, but still the efficiency was low, and at times the mixing of anolyte and catholyte was so rapid that the tank actually showed a loss of effect. By sampling different parts of the anolyte and titrating with permanganate, the efficiency could be determined. The highest obtained for the whole tank was 56%, although three of the five anolyte boxes showed 100% at one time.

The lead deposited at the cathode was of a peculiar character. It was not solid, nor apparently crystalline, even under the microscope. It did not show any tendency to tree out, and make short circuits, but covered the cathodes in a felted layer, which would drop off when the layer became too thick, in say, twenty-four hours. The same kind of a lead deposit is that obtained from other solutions containing a fraction of a per cent of arsenic and antimony. As the lead was not in satisfactory shape to either build up a solid cathode or for melting, a rolling rig to pack the deposit down was made. This was not tried until the second run and then only for a time.

The anodes were given about 50 complete vibrations per minute to keep them from polarizing. A good deal of the time there was no motion as the motor driving the anode frame was difficult to regulate with the means at hand.

The difference in specific gravity of catholyte and anolyte



was only slight, during this run, but it seemed to increase as the percentage of lead in the anolyte diminished. Catholyte with 28 grams ferrous iron per liter, had a density of 1.132 at 36°, while anolyte with 7.3 grams ferrous iron had a density of 1.144.

Some slime of Lot 2 was treated during this run by anolyte taken from the ferric-iron tank. The slime was stirred up in a barrel with a slighter excess of ferric iron, calculated as follows:

1 part copper	requires 1.76 parts Fe'''
1 " antimony	" 1.4 " "
1 " arsenic	" 2.23 " "
1 " bismuth	" 0.81 " "
1 " lead	" 0.54 " "

The solution after settling was siphoned off and agitated with a small quantity of fresh slime to reduce any ferric iron or precipitate any silver in solution. The solution was then settled and run through a filter into a tub which fed the electrolytic tanks. The slime after treatment with the solution left only a small volume of a dense metallic residue, of far less bulk than the slime treated. It filtered fairly well with cold water, and washed rapidly with hot water.

The residue was analyzed and found to contain lead 11.4%, antimony 14.1%, arsenic 1.48%, Bi 0.54%. The silver by solution in nitric acid and titration with  $\text{NH}_4\text{CNS}$  was 58.3%, a little less than the actual amount. For quick determinations to control the process this method was used however. Taking silver in the original slime at 16.2%, obtained by the same method, and assuming that no silver was dissolved, the results are given in Table 125.

TABLE 125.

	In 13 Lbs. Wet Slime.	In 1.9 Lbs. Dry Residue.	Extracted.
Antimony .....	2.67 lbs.	0.27 lbs.	90%
Copper .....	0.15 lbs.	none	100%
Arsenic .....	0.96 lbs.	0.03 lbs.	97%
Silver .....	1.11 lbs.	1.11 lbs.	none
Bismuth .....	0.18 lbs.	0.01 lbs.	94%
Lead .....	0.68 lbs.	0.22 lbs.	68%

The solution from the slime treatment was partly passed into the series of electrolytic tanks, but mostly stored and used in the second run.

The somewhat inferior results in extraction were probably due in part to the low temperature at which the slime treatment was conducted, namely, 12°–13° C. In the following run the temperature was 25°–30° C.

A test was made on one-half barrellful of solution with the proper addition of slime, to see if there was any increase in the percentage of  $\text{SiF}_6$  in the solution. It had been thought that the slime contained in an unrecoverable form products of the fluosilicic acid used in refining the lead. Very careful analyses before and after adding the slime showed no change in the amount of  $\text{SiF}_6$  present. Very little could have been in the final residue, so that with well-washed slime there is no appreciable quantity of fluosilicic acid or decomposition products left in the slime from lead refining.

At the end of the run none of the tanks had given satisfaction. There was difficulty keeping the contacts in condition on the copper tanks, because the electrodes were very light. No pure copper was produced, and much pure antimony had been converted into impure metal.

No good antimony had been made in the antimony tanks,

but the varying current density and composition and rate of feed of solution were so difficult to have controlled by my assistants before it was thoroughly understood what was required, that anything different from a collection of all kinds of deposits on each electrode could not have been expected. The iron tank had failed because of internal leaks.

The experimental plant was then shut down and altered in many respects. The contacts were improved, new and more powerful stirrers put in each tank, and the capacity of the antimony-depositing tanks increased 66%.

The ferric-iron tank was taken apart, and the anolyte boxes tested by filling them with water, and all poorly set buttons taken out. Even after that fears were entertained lest the wood should expand or contract by wetting or drying and loosen the buttons. The plan of mounting the buttons in hard rubber plates by means of soft rubber rings cut from a rubber tube surrounding each button was considered, but it was thought to require too much time. To make sure of the successful operation of the tank, so that the process itself could be thoroughly tested, each anolyte box was covered with a double layer of cotton duck. The duck was so successful in withstanding the action of the solution, that it will undoubtedly itself provide a suitable and economical diaphragm if the tank is so constructed that new sheets of duck may be substituted every month, say, and without its being necessary to take the tank itself apart.

For the second run, the old solutions were analyzed before mixing, with results as in Table 126.



TABLE 126.

	Lead.	Iron.	SiF <sub>6</sub> .	Antimony.
Fresh solution .....	0.57	2.14	14.5	
Old catholyte .....	1.13	3.08	12.8	0.32
Old anolyte after adding slime .....	1.04	3.03	10.9	1.46
Old solution from antimony tanks ...	3.18	2.72	12.1	0.65
Old solution ready for depositing tanks	1.48	2.96	11.3	0.88

The mixed solution used contained about 2.85% Fe and 12.6% SiF<sub>6</sub> and was maintained at about this strength throughout the run. The amount of HF present was not determined, but was not far from one per cent. The solution was entirely too weak for the best results, and was low in free acid, averaging about 1 or 2% only. What acid was not combined with ferrous iron was combined with lead, or the whole was combined with ferric iron. If the solution had contained more free acid, the power consumption on the iron tank would have been much less. It is rather surprising that such good results were obtained with such a weak solution. It had been intended to work with 16% SiF<sub>6</sub>, but one of the barrels in which acid had been stored had leaked out.

In starting up, the first tanks to be put in operation were the copper-depositing tanks and one of the antimony-depositing tanks. As the solution gradually filled the other tanks the current was increased. After twenty-four hours the iron tank at the end contained 4 inches of solution. As it filled the current was increased, keeping the voltage practically constant at 3.5 volts. The current reached 160 amperes after about 70 hours and the full 300 amperes was not reached for eight days.

The tank could have taken the full current earlier, but was in series with the antimony and lead-arsenic depositing

tanks, and the current was kept down in an attempt to get the desired pure antimony deposition. At that time the other tanks had been finally taken out, and thereafter the iron tank only was operated.

The copper-depositing tanks did not give good results at any time, partly because the contacts were poor, and the current density on some electrodes was in consequence far too high. I scraped the deposits from two cathodes, one with a heavy deposit and the other with a light one. After melting they gave on analysis the figures in Table 127.

TABLE 127.

	Lead.	Copper.	Bismuth.	Antimony.	Arsenic.
Heavy deposit .....	3.57%	4.15%	1.0%	74.6%	14.2%
Light deposit .....	1.9 %	10.5 %	5.1%	69.6%	13.7%

There were five antimony-depositing tanks on this run, instead of three as before. The highest current density used was about 6 amperes per square foot. Some of the best looking deposit contained 8.15% lead, so it was apparent that the most vigorous circulation and close regulation would be necessary for the successful production of antimony.

The arsenic-lead depositing tanks gave nearly continuously a soft deposit of lead.

After a few days running the copper tanks were found to be allowing copper to pass through them, and they were disconnected and replaced by a box containing metal scraped from the cathodes in the antimony-depositing tanks. This box was 11 inches by 14 inches and the layer of metal which rested on a false bottom was about 3 inches thick. The solution ran through too rapidly when the box was filled, and the

copper was not all removed. From the analyses in Table 128, it will be seen that the lead in the box dissolved away first, precipitating antimony and copper, while later the antimony dissolved and copper precipitated.

TABLE 128.

Day of Run.	Solution Fed to Copper Extractor.			Solution Flowing from Copper Extractor.		
	Cu	Sb	Pb	Cu	Sb	Pb
5th .....	0.075%	1.35%	1.48%	0.04%		
7th .....	0.086%	1.65%	1.77%	0.04%	1.54%	1.78%
8th .....		1.70%			1.75%	
9th .....		1.80%		0.044%	1.80%	
11th .....				0.01%		
12th .....				0.012%		
13th .....				0.017%		

Better results would have been obtained if the box had been filled with lead from the ferric-iron tank. This would have a finely divided form and be more active than the more solid metal that was used. With an arrangement such that the overflow of the box had been high enough to keep the precipitating metal always flooded, and the flow of solution had been uniform, instead of intermittent, better results would have been obtained.

Tests were then made to determine whether antimony and arsenic could be precipitated by lead in a similar manner. The cathode lead in the ferric-iron tank, which was being packed down on the cathodes by rolling, was tried in the test. This material was found to analyze at two different times as follows:



TABLE 129.

Sb.....	.46%	.30%
As.....	.47%	.29%

It consists of fine particles of lead loosely held together, with no crystallization apparent under a small microscope. It deposits in a felted layer on the cathodes and for use in precipitating was wiped from the cathodes by means of a trowel into a long tray resting on top of the tank.

A layer of this lead about three-fourths of an inch thick was put in a funnel and solution from slime treatment rapidly run through, with results as given in Table 130.

TABLE 130.

	Solution.	Filtrate.	Soft Material Left on Filter
As.....	0.44%	0.18%	6.7%
Sb.....	1.50%	0.87%	24%
Pb.....	2.08%	6.9%	

The layer of precipitating lead was too thin and the speed of flow was rapid, so a complete extraction of antimony and arsenic was not expected. The solution used contained some pentavalent antimony, which is not precipitable.

After a number of other similar tests were made which showed a ready precipitation of arsenic and antimony by the cathode lead, the solution running from the copper extractor described above, already in use for two or three days, was passed through a 11-inch by 14-inch box containing a layer of cathode lead several inches thick, resting on a false bottom. The solution running through contained 0.07% As and 0.44% Sb. The antimony in the run-off came down with  $H_2S$  only after a long time and with difficulty, showing that it was present in the solution as pentavalent antimony.

After some eighteen hours the solution running through began to contain more antimony, roughly determined by titrating 10 c.c. with permanganate solution, so another smaller box 7×7 inches with a layer of lead about 3 inches thick was put on just above the original box. All the electrolytic tanks except the main tank were emptied and their contents poured through with the solution coming from the slime treatment.

The solutions running through the boxes were sampled every two hours for several days, and the samples analyzed for iron, antimony, and arsenic. It would take space unnecessarily to give all the results, but they showed a very good extraction of arsenic, and extraction of practically all the precipitable antimony, when sufficient lead was in the precipitating boxes.

The solution still contained about 0.6% of antimony in the pentavalent condition, a result of either the high voltage developed at times in the antimony and lead-arsenic tanks, or of oxidation in some of the compartments of the ferric-iron tank, when the supply of ferrous iron was exhausted from insufficient circulation. I had another unfavorable condition to contend with in not having a sufficient stock of cathode lead on hand to fairly fill the precipitating boxes, as a result of which the lead in the boxes was at times practically exhausted before I had collected enough from the tank to fill them, while some was wasted as we were compelled to work. Practically the amount of lead taken from the electrolytic tank exceeds the amount dissolved from the precipitating boxes, because some lead is always coming into the system in the slime being added, but it is evident that it is necessary to have a certain stock on hand in the precipitating boxes, if all or nearly all of the antimony and arsenic is to be precipitated. What escapes, if any, has still to be electrolyzed

near the cathodes of the electrolytic tanks, when it is largely removed in the cathode lead.

The favorable condition of the cathode lead as a precipitating material was due to the solution being somewhat impure in respect to antimony and arsenic, so with a complete extraction of these elements in the precipitating boxes, it would be necessary to run into the electrolytic tank a little solution still containing arsenic and antimony.

The ferric-iron tank produced about 60 lbs. of granular lead daily, which was removed from the cathodes every 12 or 18 hours and shoveled into precipitating boxes, of which there were eventually four in series. I sampled the four successive layers of one box which had been taken out, with the results given in Table 131.

TABLE 131.

Layer.	Lead.	Copper.	Antimony.	Arsenic.
Top .....	none	present	47%	25%
No.2 .....	none	.....	42%	45%
No. 3 .....	.....	.....	28%	62%
Bottom .....	.....	.....	13.2%	40.5%

Of the four boxes in series, and while they were still operating efficiently, I took samples as follows: Box A was  $7 \times 7$  ins. and contained a layer about 4 ins. deep. Sample  $A_1$  was the top quarter, and  $A_2$ ,  $A_3$ , and  $A_4$  the following quarters. Box B was  $11 \times 14$  ins. and contained a layer about  $5\frac{1}{2}$  ins. deep. Samples  $B_1$  to  $B_5$  were of the five successive inch layers from top downwards. C was a pail  $10\frac{1}{2}$  ins. diameter at the top and 8 ins. diameter at the bottom, and had a layer about 4 ins. thick. Samples  $C_1$  to  $C_5$  are of the five successive layers from the top down. Box D was  $11 \times 9$  ins. and contained a



layer  $9\frac{1}{2}$  ins. deep. Samples  $D_1$  to  $D_4$  are from the four layers of equal depth. The analyses were hurried and the bismuth determinations were not satisfactory. In a general way, samples  $C_1$  and  $C_2$  contained the most bismuth and a good deal of it, especially  $C_1$ .  $C_3$  is an accurate analysis by Mr. A. E. Knorr. The results are given in Table 132.

TABLE 132.

Number.	Cu, Per Cent.	Bi, Per Cent.	Pb, Per Cent.	Sb, Per Cent.	As, Per Cent.	Of Total Volume.
$A_1$ .....	40.2	none	trace	35.7	9.9	2.3%
$A_2$ .....	38.2	none	none	41.8	12.3	2.3%
$A_3$ .....	.....	.....	trace	52.5	13.4	2.3%
$A_4$ .....	24.3	trace	trace	51.0	16.7	2.3%
$B_1$ .....	2.5	none	none	52.5 ?	.....	8.0%
$B_2$ .....	.....	.....	.....	64.5	24.0	8.0%
$B_3$ .....	none	none	none	62.3	25.1	8.0%
$B_4$ .....	none	.....	none	68.2	23.1	8.0%
$B_5$ .....	none	none	none	57.5	25.7	8.0%
$C_1$ .....	0.75	33% by difference 13% by difference	2.0	38.5	25.7	2.4%
$C_2$ .....	none					
$C_3$ .....	none	10.9	2.5	59.5	23.2	2.2%
$C_4$ .....	trace	2.2	2.0	43.9 ?	14.6	2.1%
$C_5$ .....	none	2.7 ?	.....	62.2	19.9	2.1%
$D_1$ .....	none	trace	13%	56.6	13.7	9.9%
$D_2$ .....	none	none	12	.....	13.6	9.9%
$D_3$ .....	none	none	13	64.5	11.1 ?	9.9%
$D_4$ .....	none	none	32.3	61.7	.....	9.9%

There are evidently three distinct products, the first of which contains nearly all the copper, and would probably contain all the copper with a better arranged set of precipitating tanks. This product, I believe, would be nearly pure copper and not a compound of copper with antimony or arsenic, as copper particles had been already formed, and it is probably only a question of time until the antimony and arsenic are all dissolved from the upper layers. This seems all the more probable since antimony and arsenic are known to precipitate

copper itself under the proper conditions. Further, the antimony and arsenic are in an ideal condition for chemical action on account of the fine division of the particles resulting originally from their precipitation from solution, by lead particles. The complete absence of lead from this product and the following one is fortunate. Whether the copper product assayed 40% or more, it would probably go to a copper anode furnace anyway.

Bismuth is first found on going through the mass from the top downward, when the first layers containing lead are reached, and no other conclusion is possible, except that the bismuth in the solution run in is precipitated by lead and not by copper, antimony, or arsenic, and also that antimony and arsenic are precipitated by bismuth already precipitated itself by lead, while the bismuth redissolves and passes further down until it comes into contact with metallic lead again. The bismuth must pass unprecipitated through the copper layers and the antimony-arsenic layers and be precipitated in the first lead. As this lead dissolves away in precipitating arsenic and antimony, the bismuth must dissolve with it only while the lead continues in solution and flows away, the bismuth is almost immediately again reprecipitated. Given a mass of precipitating lead into which the slime solution flows, the longer the time allowed, the wider will be the respective bands, and probably the higher will be the percentage of copper in the copper product and of bismuth in the bismuth product. Whether the bismuth layer would become in part at least pure bismuth is uncertain, but it makes very little difference as we have a simple and practical method of treatment. This is by stirring the product into the same solution as is used for treating slime, when the bismuth, being now more concentrated than in the slime,

will separate for the most part as insoluble bismuth fluoride, while antimony, arsenic, and lead dissolve, and the solution may be passed through the precipitating boxes with the slime solution.

The principal product, in quantity at least, is the arsenic-antimony layer. This is fortunately free from lead. It shows no disposition to separate into two layers, one of antimony and the other of arsenic. This I proved by taking another sample, several days later, from the same locality that sample  $B_1$  was taken. It contains Sb 61%, As 26.7%. The proportion of the two metals is almost exactly the same as the proportion in which they are removed from the slime.

At this time I have not yet had the opportunity of testing methods of recovering the antimony. If simply heated and melted in a crucible the product contains 17.2% As, and by further treating in a carbon crucible nearly to a white heat the arsenic is reduced to 8.7%. Exposing the melted metal to air does no good. 37.5 grams of alloy containing 8.7% arsenic was reduced by oxidation to 31 grams, but arsenic was still as high as 7.6%. Taking account of the vast difference in the boiling-points of metallic arsenic and antimony, and the absence of any strong combination between the two, sufficient heating of the antimony ought to give a complete separation. Possibly also by partial oxidation under the proper furnace conditions the arsenic can be got off as  $As_2O_3$  and the antimony left as metal. I expect to try heating the metal to the boiling-point of antimony in a carbon crucible placed in an electric furnace. Arsenic may be removed by treatment with sulphur.

The various products can be distinguished by their appearance. The copper product is a black mud, the antimony-arsenic product is, when stirred with water in a glass vessel,



flaky like mica, and brilliant, while the bismuth product is intermediate between the antimony-arsenic product and the unchanged lead.

The slime treatment itself was carried out in barrels, the method being to stir into the warm anolyte, containing about 2.5% of ferric iron as it came from the electrolytic plant, a batch of slime that had been already used to reduce any excess of ferric iron left in the solution after treatment of the previous batch. The slime and solution were stirred generally for about half an hour, using with our weak solution about  $2\frac{1}{4}$  cubic feet of solution for a 6-lb. lot of slime. After settling half an hour, the solution was decanted to another barrel with no silver or merely a trace in solution, and in one case when a test was made 0.16 gram of solid material per litre. To the decanted solution a fresh lot of slime was added to reduce any ferric iron. In this way each lot of slime and each lot of solution was treated twice, so that the slime was thoroughly treated and the solution thoroughly reduced without its being required to get the exact quantities necessary for each treatment. If we were using too much slime the titration of the solution, after being put on slime for the first time, would rise with each batch, when the size of the slime lots could be diminished. Some 45 lots were treated altogether, of which the first were removed separately while the last one-half or so were allowed to accumulate in the slime-treating barrel. The various lots were sampled and analyzed for silver by dissolving in nitric acid and titrating with  $\text{NH}_4\text{CNS}$  solution. The results by this method, when checked up, were found a little low, say 1 to 3%. The figures are given in Table 133.

TABLE 133.

Lot.	Per Cent Silver.	Lot.	Per Cent Silver.	Lot.	Per Cent Silver.
5.....	56.4	17	62.9	28	67.2
6.....	54.7	18	67.1	29	
7.....	40.0	19	62.9	30	
9.....	65.7	20	63.6	31	
10.....	61.3	21	59.6	28	67.4
11.....	61.9	22	57.3	to	
12.....	57.8	23	60.3	41	
13.....	53.4	24	56.2	42	
14.....	61.6	25	61.8	to	54
15 and 16.....	65.9	26	56.3	54	
16.....	63.1	27	61.8		

The low percentage of silver in some few lots was due to the use of too much slime for a given amount of solution. An accurate analysis by Mr. A. E. Knorr gave for the original slime the figures given in Table 134. Our figures for Lot 28 to 41 by his method and the percentages of extraction, on the assumption that the weights are inversely proportional to the percentages of silver, are also given.

TABLE 134.

	Raw Slime.	Treated Slime.	Percentage of Extraction.
Silver.....	17.2%	67.4%	0.0
Bismuth.....	2.6%	0.3%	97.0
Copper.....	2.45%	0.2%	97.9
Lead.....	11.9%	7.8%	83.1
Antimony.....	39.2%	10.0%	93.4
Arsenic.....	16.0%	0.43%	99.3
Tellurium.....	1.3%	2.12%	?

Other analyses of treated slime are given in Table 135.

TABLE 135.

Lot.	Lead.	Silver.	Copper.	Arsenic.	Antimony.	Bismuth.
5.....	8.3%	56.4%	none	2.1%	16.0%	7.4%
6.....	8.5%	54.7%	none	1.2%	11.5%	5.2%
7.....	15.6%	40.0%	none	1.4%	16.4%	3.2%
9.....	5.2%	65.7%	none	0.5%	18.0%	1.0%
10.....	7.4%	61.3%	none	2.1%	15.2%	3.9%

These early lots are not as representative of the process as the later combined lots.

Regarding the percentage of extraction of the various metals there could be considerable variation even if there was complete oxidation by ferric iron. If the solution contained too much hydrofluoric acid the extraction of lead would be adversely affected, as lead fluoride could separate in the slime. In this case also the percentage of bismuth extracted would be a minimum. On the other hand if the solution contained too little HF antimony would remain in the slime as trioxide in large quantities. In this case bismuth would be largely or entirely removed as fluosilicate. My results indicate that there is a safe mean between the two extremes. A ready method of control is to dissolve a sample of the treated slime in concentrated  $\text{H}_2\text{SO}_4$ , dilute to 500 c.c., add 50 cc.  $\text{HCl}$ , and titrate with permanganate for a rough antimony titration. If antimony is too high add a little more HF.

From the standpoint of metal recovery, the extractions were pretty satisfactory, though it would be better if the silver residue was left in a purer condition. By the use of stronger and warmer solutions there would be an improvement to some extent at least, and longer agitation of slime with solution would probably help. Theoretically there is no reason why practically all the base metals could not be



removed, and possibly even tellurium could be removed and recovered by a certain procedure.

The residue from the slime treatment is dense and solid and occupies a very small fraction of the space occupied by the raw slime itself. It filters rather slowly in the cold, but washes rapidly with hot water.

Arsenic fumes were noted for a few hours during the first run, but no arsenic was evolved from the solution or apparatus after the copper, antimony, and lead-arsenic depositing tanks were cut out.

For a commercial plant the following points are worth considering.

The electrolytic tanks for depositing lead and producing ferric iron could use diaphragms of cotton duck stretched on wooden frames. The frames should surround the cathodes and not the anodes, as in my apparatus, because when renewals are required, which would probably be about once a month, the cathodes are more easily removed than the anodes. The frames or boxes would be pulled out, new duck stretched on and replaced. These boxes should be open at the bottom, and not quite reach the bottom of the tank. The heavy anolyte lying in the bottom of the tanks would dissolve any soft lead falling from the cathodes and prevent a troublesome accumulation, without affecting the cathodes, provided they did not reach too low in the tank. The anolyte with this construction could be readily circulated throughout the tank, a very desirable thing. The cathodes should best be of copper sheet and the tanks should be served by a crane so that the cathodes could be lifted out and away every twelve hours and the lead wiped off by the tank load, an operation that would take but a few minutes with apparatus like that shown on page 245.

The feed of solution would be divided as equally as possible between the cathode compartments, while the discharge would be merely through an overflow hose. A current density of 10 amperes would probably be near the upper limit if it was desired to oxidize most of the ferrous iron. The voltage would be about two volts.

The slime treatment probably need not be conducted in separate batches of regulated size. A whole day's production of slime could probably be placed in one tank, and anolyte from the tank allowed to collect there for perhaps an hour, when it could be stirred and settled and the solution passed to the precipitating boxes. In this way the lead and bismuth might be removed first and the copper last, but as the precipitation of the metals is automatic there is no necessity for a constant composition of solution passing through the precipitators.

The precipitation boxes should all have downward percolation because the outflowing solution, containing more lead, is heavier than the inflowing. A little consideration shows that the metals should stratify horizontally under these conditions. By skilful regulation it is probable that the different products could be collected in separate boxes if desired. If not the different layers could be detected by the different appearance. The washing ought to be easy, if water is added at the top to displace the heavier solution, for the material is of a very open, pervious nature. The material in the boxes would be kept flooded at all times except when unloading by having the discharge at a level about the same as that of the top of the material. The resistance of the metal to the flow of the solution is very slight and is hardly to be considered.

The solution flowed through one of the boxes in my experiment at the rate of 40 inches per hour, which was far too high. A speed of 4 inches per hour would not make the size of the precipitating tanks inconveniently large at all, and would give a better chance for the reactions to occur at the proper place, and would not allow the different metals to get beyond their respective zones of precipitation.

The control of the process would be by titrating samples of the solution flowing from the electrolytic tanks by standard permanganate solution. The action on the slime can be followed in the same way.

For following the operation of the precipitating tanks, titrating the inflowing and outflowing solution by permanganate, or taking the specific gravity of each, should give the desired information. In these titrations the permanganate oxidizes antimony and iron both, and will certainly oxidize arsenic in presence of  $\text{HCl}$ , and probably in presence of  $\text{H}_2\text{SO}_4$ .

If the slime-treating solution accumulates lead fluosilicate, on account of the use of slime not thoroughly washed, an electrolytic method exists for taking this out again in the form of pure lead fluosilicate.





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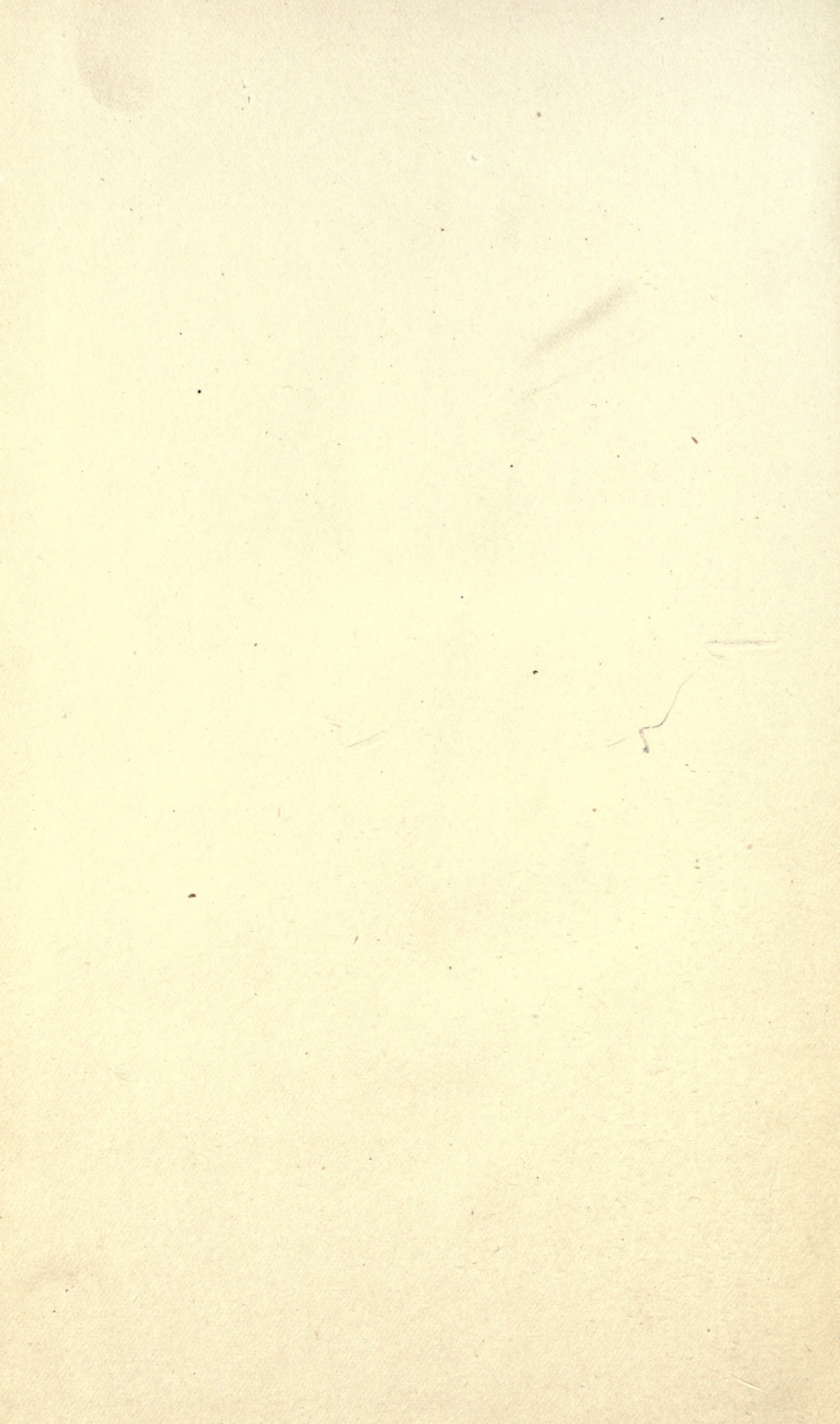














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